

Applications of 2,4-Dioxo-3-oxabicyclo[3.2.0]-
hept-6-ene as a Synthetic Equivalent of
Acetylene and of Cyclobutadiene

by

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Thesis presented for the degree of
Doctor of Philosophy

University of Edinburgh

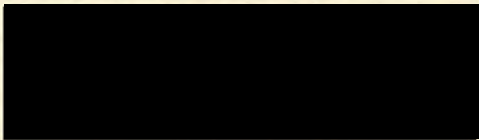
January 1985



Declaration

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes the results of research carried out in the Department of Chemistry, University of Edinburgh under the supervision of Dr. I. Gosney since 1st October 1980, the date of my admission as a research student.



Postgraduate Lecture Courses

The following is a statement of the course attended during the period of research.

Organic Research Seminars (3 years attendance).

Current Topics in Organic Chemistry, various lecturers (15 lectures).

Homogenous Catalysis, Dr. T.A. Stephenson (5 lectures).

Bio-organic Chemistry, various lecturers (5 lectures).

1,3-Dipoles in Organic Synthesis, Dr. J.T. Sharp and Dr. R.M. Paton (5 lectures).

Modern Synthetic Methods in Organic Chemistry, Dr. G. Tennant (5 lectures).

Molecular Interactions in Industrial Food Research
Unilever Research (5 lectures).

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Finally, I would like to express my gratitude to Professor J.I.G. Cadogan for his guidance and interest and to British Petroleum for financial support.

Abstract

The preparation and flash vacuum pyrolysis (FVP) of derivatives of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene has been extensively investigated. In some instances, a retro-Diels-Alder reaction was observed with loss of maleic anhydride thus illustrating the ability of this alkene to serve as an acetylene synthon. As part of these studies 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene was synthesised by a novel route and its reactivity studied. FVP of adducts formed with this reactive alkene showed that in some cases it functioned as a cyclobutadiene synthon by elimination of anthracene. However with other adducts the alkene acted as an acetylene synthon with pyrolytic loss of dibenzobarrelene. Under similar conditions adducts of 5,6:7,8-dibenzobicyclo[2.2.2]octa-²₅,7-triene (dibenzobarrelene) are found to eliminate anthracene thus demonstrating dibenzobarrelene as an acetylene synthon.

7,8:9,10-Dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene is also observed to undergo polymerisation by metathesis. When subjected to heating, the thermal elimination of product loses anthracene to form poly(acetylene), a polymer of current interest in the field of conducting polymers.

3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide showed little activity as an acetylene synthon but, interestingly, its adduct with tetracyclone formed a novel dihydrosemibullvalene when subjected to pyrolysis under FVP conditions.

By successive α -chlorination and treatment with base, 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide was converted into

Dewar benzene which was trapped as its tetrabromide derivative as evidenced by mass spectroscopy.

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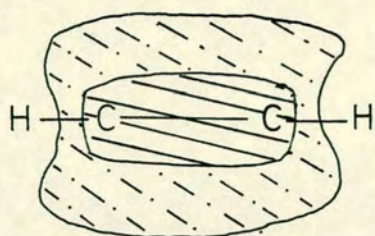
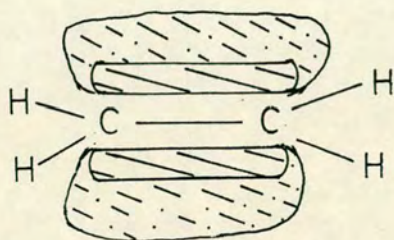
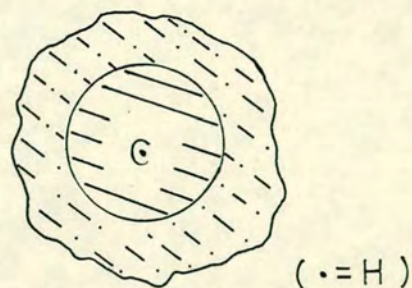
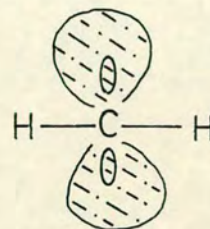
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A. Acetylene equivalents

Conceptually the use of acetylene as a dienophile or a 1,3-dipolarophile provides a useful way of synthesising 1,4-cyclohexadienes (Diels-Alder reactions) and olefinic five-membered rings respectively, but such cycloaddition reactions have been found difficult to perform experimentally for two main reasons, (i) the safety hazards¹ involved in the use of acetylene at the necessary elevated temperatures and pressures, and (ii) the lack of reactivity shown by acetylene.²

In general, the carbon-carbon triple bond is much less reactive than a carbon-carbon double bond and acetylene shows a surprising lack of reactivity in cycloaddition reactions despite the obvious structural similarities between the two unsaturated groupings. A consideration of the structural bonding in both types of species helps to explain this phenomenon.

In the case of acetylene itself the accepted structure consists of two sp-hybridised carbon atoms and two hydrogen atoms. One sp hybrid orbital from each carbon overlaps the s orbital of its hydrogen atom to form a σ bond. The other sp orbitals overlap each other endwise whilst the two remaining unhybridised p orbitals from each carbon form π bonds.³ A triple bond is thus composed of one σ and two π orbitals. The density distribution of the π electrons in the acetylenic bond is illustrated in fig 1 a and can be represented as a cylindrical cloud of electrons which overlaps and extends past the carbon atoms.

fig 1afig 1b

On the other hand, in the ethylenic bond π -electrons are not delocalised to the same extent. In fact the density distribution in ethylene can be pictured as two rods, one above and one below the carbon atoms as shown in diagram (fig 1b).

In spite of the higher electron density associated with the carbon-carbon triple bond, the electrons are held more tightly because of the smaller carbon-carbon bond distance. This explains why acetylene reacts only with electron rich dienes under severe conditions.⁴

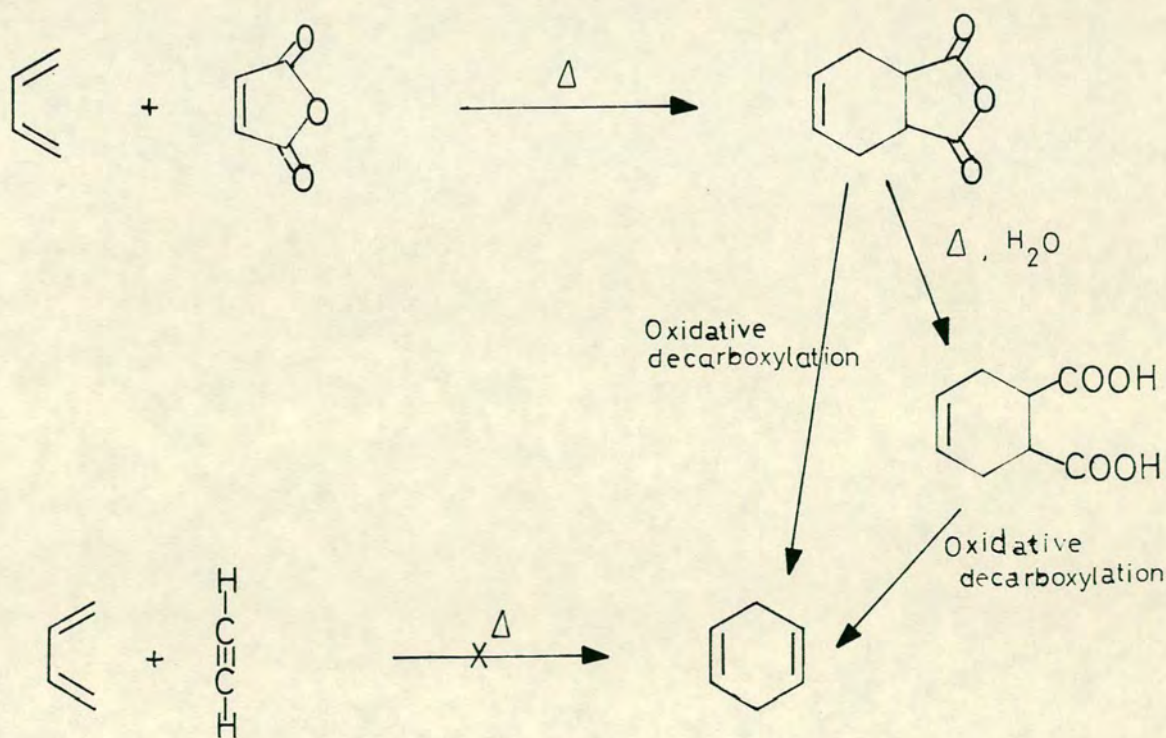
Due to the lack of reactivity of acetylene in cycloaddition reactions there has been a sustained interest over the last two decades in developing procedures which are equivalent to the use of acetylene as a dienophile, thereby giving general access to cyclic alkenes. Such compounds are generally referred to as acetylene equivalents or acetylene synthons.

A number of such molecules have been designed, which

circumvent the aforementioned problems. Many of these are selective and some require severe reaction conditions, although recently, several synthons have been discovered that are more versatile and require much milder conditions. These reagents are now discussed from a historical perspective beginning with maleic anhydride.

1. The use of maleic anhydride as an acetylene equivalent

Maleic anhydride shows considerable utility as a dienophile and has long been used as an acetylene equivalent by means of simple oxidative decarboxylation of its readily formed adducts. This strategy is outlined in Scheme 1.



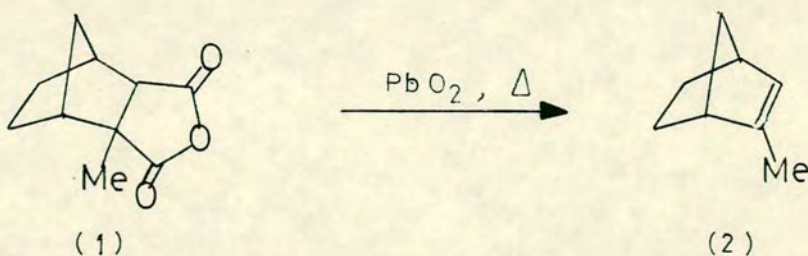
Scheme 1

Several reagents have been used to effect the oxidative decarboxylation of maleic anhydride adducts but all of them possess certain disadvantages as detailed below which make them

inappropriate for use with particular types of anhydrides or diacids.

a. Oxidative decarboxylation with lead dioxide

Lead dioxide was first used as an oxidative decarboxylation agent for diacids and anhydrides^{5,6} in the early 20th century. The method usually involved heating of the adduct with lead dioxide at 200°C, often without solvent, and led to extensive decomposition giving only low yields of product. The low yields were probably due to the further oxidation of the generated alkenes by Pb^{IV}. A later report⁷ indicated that the yields were not reproducible and seemed to be very much dependent upon the method of preparation of the lead dioxide. Despite these limitations several successful syntheses of some bicyclic alkenes have been reported, such as the decarboxylation of anhydride (1) to the strained alkene (2).⁸

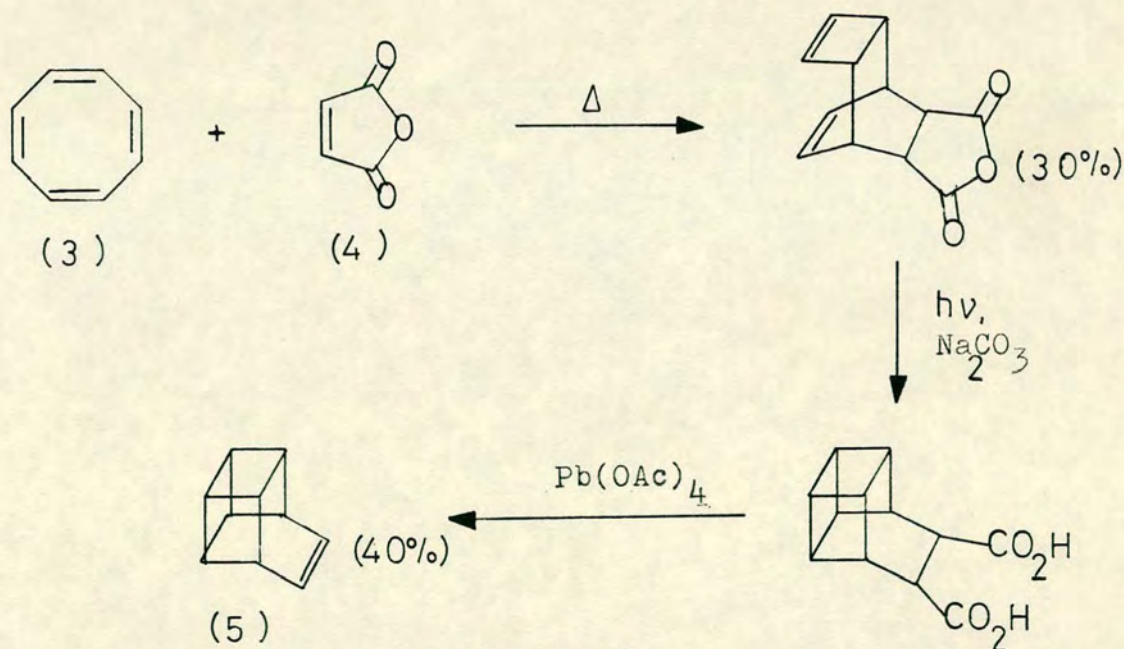


b. Oxidative decarboxylation with lead tetraacetate

In 1958 Grob⁹ suggested that the use of lead tetraacetate in benzene or acetonitrile at reflux temperatures in the presence of an organic base such as pyridine could give improved yields (up to 50%) in oxidative decarboxylations; a further modification involved the use of pyridine as solvent.¹⁰ Cimarusti

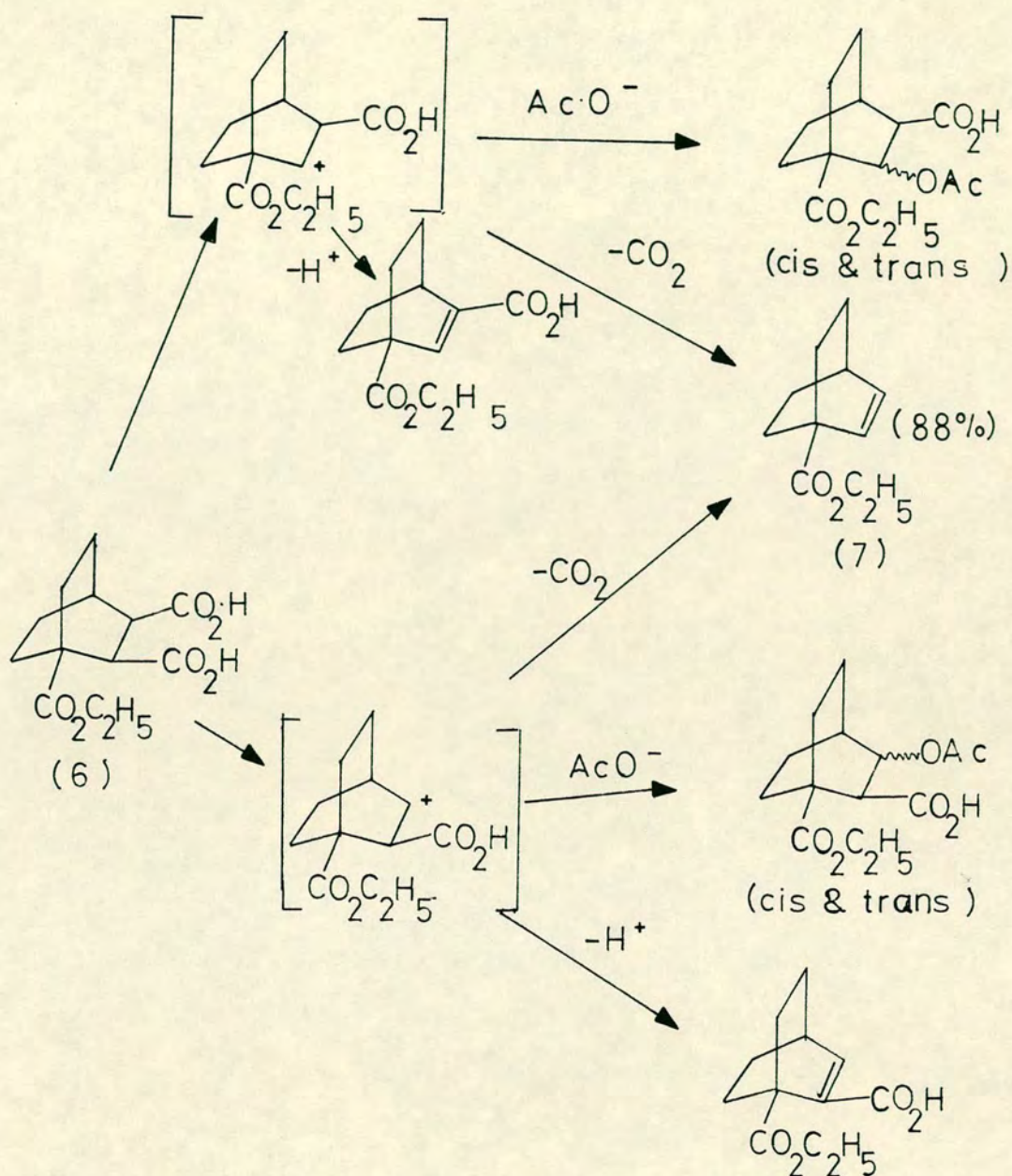
and Wolinsky^{11,12} found that the yields of alkenes formed from bis-decarboxylations were increased in the presence of oxygen and also by shortening the reaction times and increasing the amounts of lead tetraacetate. This led to a much less extreme procedure than that with lead dioxide and typically involved formation of the maleic anhydride adduct, hydrolysis, followed by oxidative bis-decarboxylation of the resulting diacid with lead tetraacetate in pyridine at 70°C.

The method is illustrated in Scheme 2 by formation of basketene¹³ (5) in 12% yield from the Diels-Alder adducts of cyclooctatetraene (3) with maleic anhydride (4).¹⁴



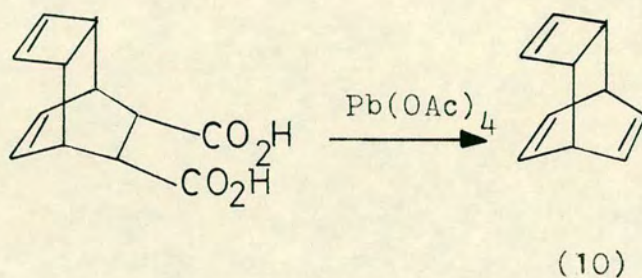
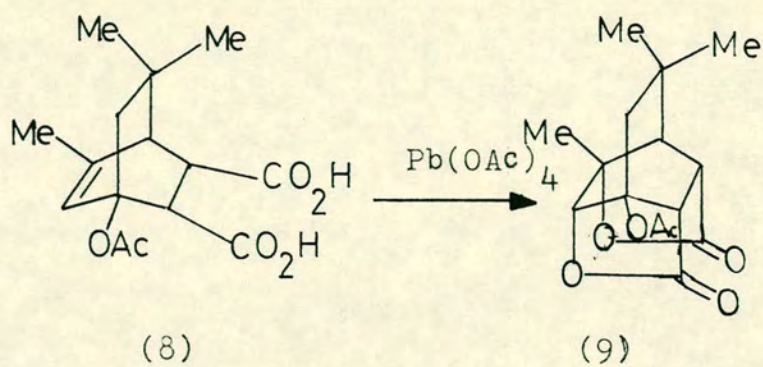
Scheme 2

Although the method gave better yields than with lead dioxide it was still far from perfect since side reactions and rearrangements often accompanied the reaction. For example, Scheme 3¹⁵ illustrates the plethora of products obtained from the decarboxylation of acid (6) to alkene (7).

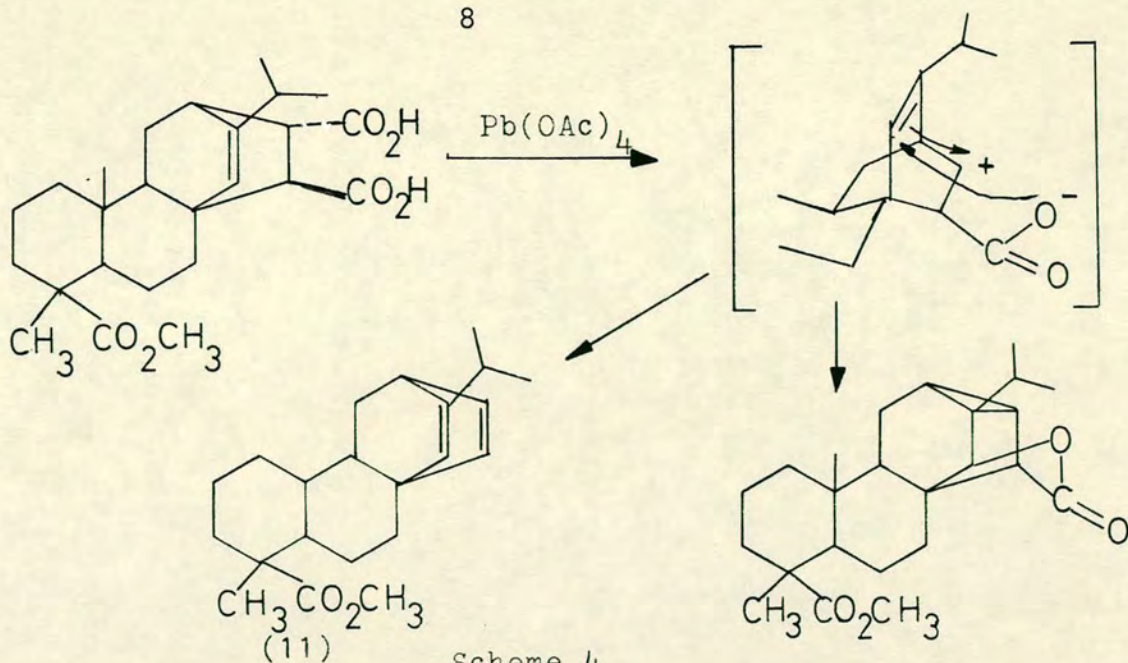


Scheme 3

Problems are also encountered when a double bond is in close proximity to the carboxyl groups. For example, the only product obtained from the diacid (8) was the dilactone (9),¹⁶ although there are a few exceptions to this generalisation such as the preparation of Nenitzescu's hydrocarbon^{17,18} (10).

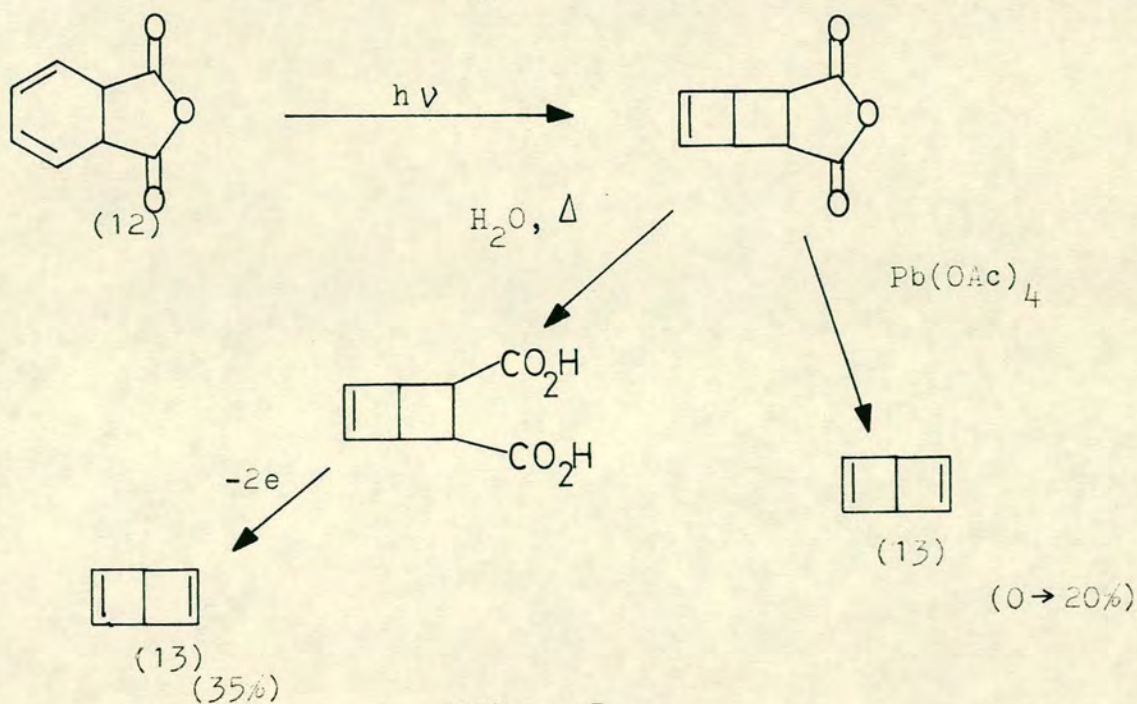


A second type of lactone formation also occurs in the oxidative decarboxylation of trans-diacids. Thus, Zalkow and Brannon¹⁹ observed a rearrangement of this type in their partial synthesis of the diene (11) as shown in Scheme 4.

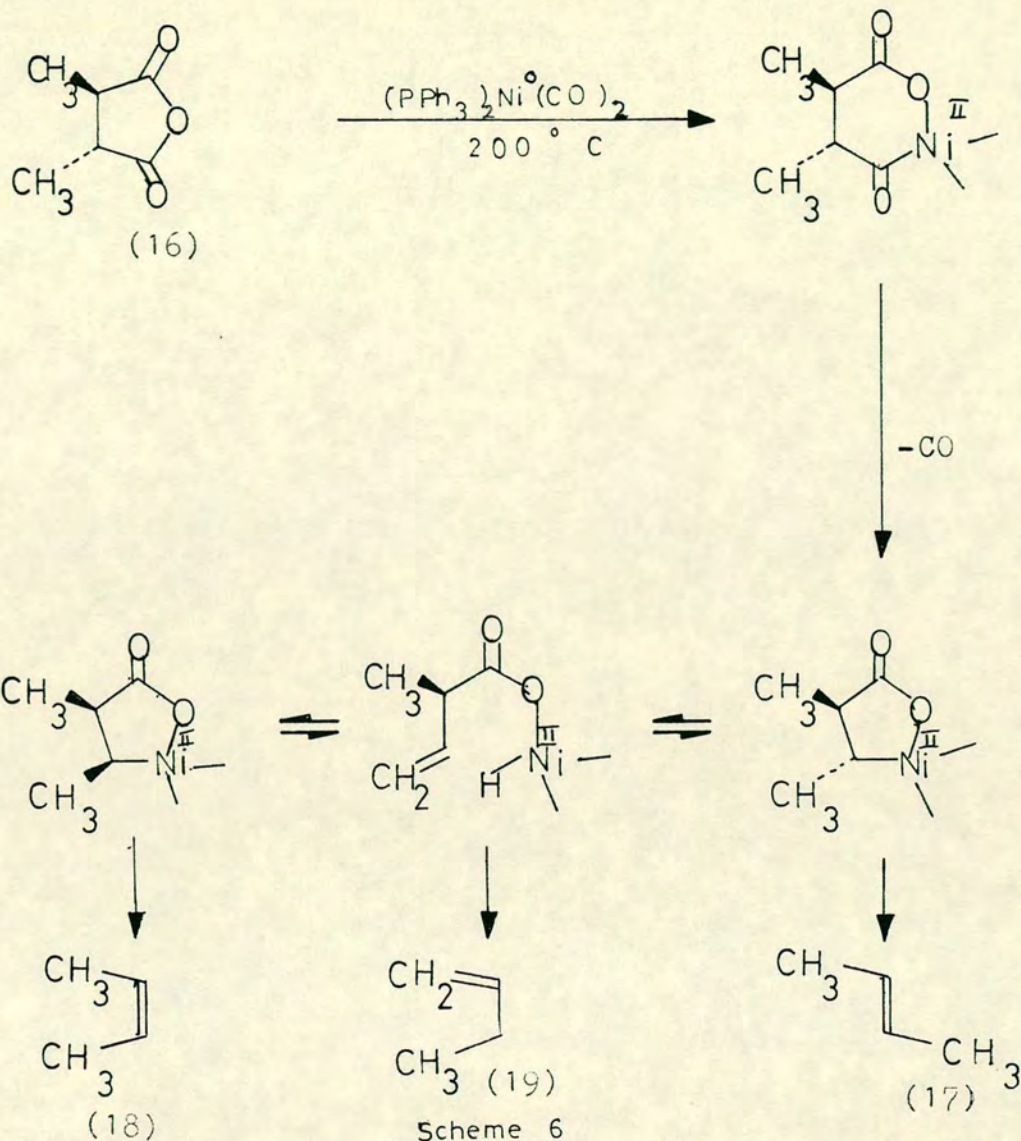


Scheme 4

In passing it is worth noting that another method for generating double bonds from maleic anhydride adducts involves decarboxylation of a diacid by electrolytic techniques.²⁰ This method was used by van Tamelen²¹ in his elegant synthesis of Dewar benzene (13) from cis-dihydrophthalic anhydride (12) and superseded the method involving decarboxylation with lead tetraacetate. The comparative reactions and yields²² are shown in Scheme 5.



Scheme 5



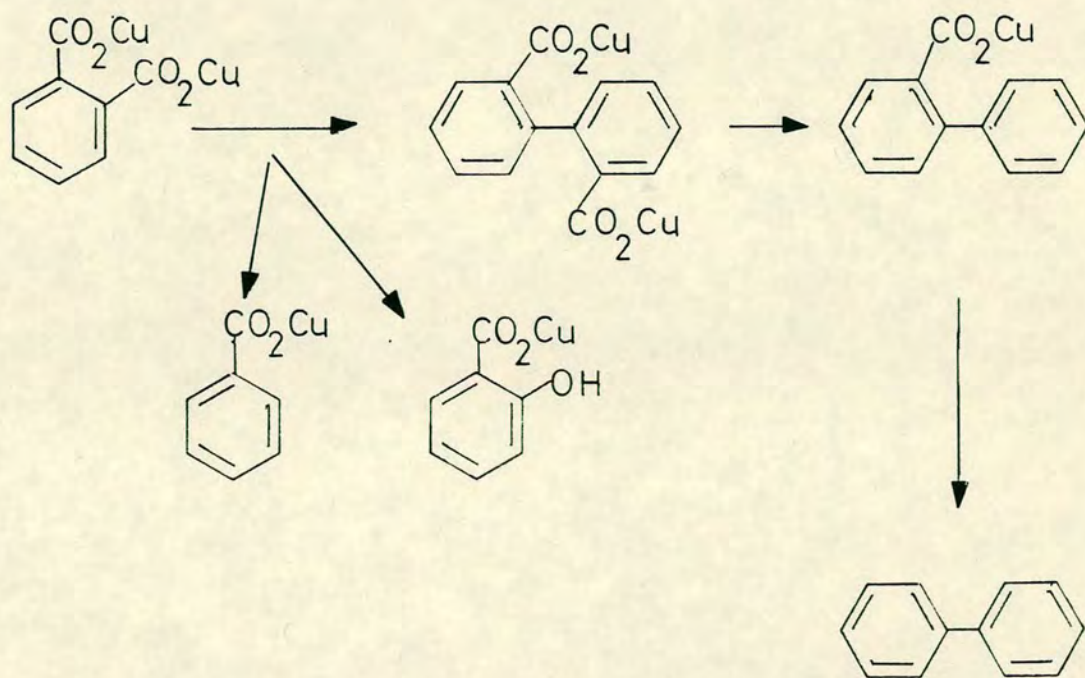
In an attempt to improve the procedure the elimination of thioanhydrides, easily obtained by treatment of the corresponding anhydride with sodium sulphide, was examined. The eliminations proceeded readily with diiron nonacarbonyl and tris-triphenylphosphine rhodium(I)chloride as well as with bis-triphenylphosphine nickel dicarbonyl and in general the yield of olefin obtained was much higher than that from the corresponding anhydride. As with anhydrides the reaction did not appear to be practical for thioanhydrides possessing an abstractable β -hydrogen.

In summary, the use of transition metal complexes for the

decarboxylation of anhydrides and thioanhydrides seems to be a useful alternative to lead tetraacetate but only when a non-abstractable β -hydrogen is present in the diacid.

d. Oxidative decarboxylation using copper(I) reagents

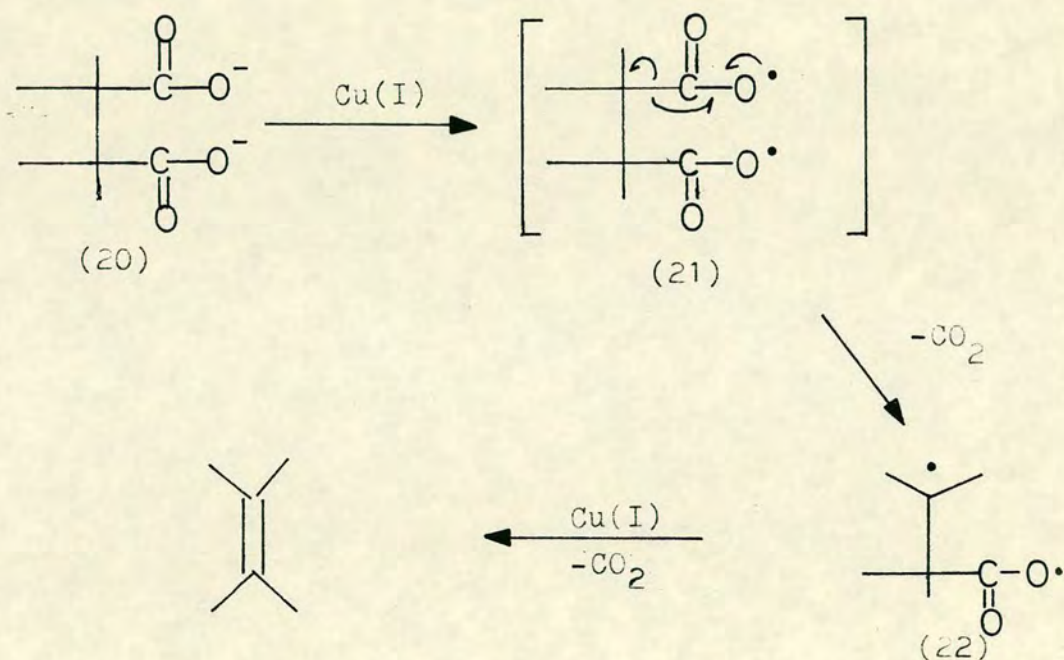
Paquette and his co-workers²⁴ have designed an alternative method of effecting bis-decarboxylation when difficulty is encountered in forming systems which showed a strong tendency to undergo structural rearrangement²⁵ e.g. (6) in the presence of lead tetraacetate. Conceptually, the procedure was designed to bypass the possible intervention of transient carbocations (such as those postulated in Scheme 3) by the use of Cu(I) reagents. Decarboxylations of aromatic acid with copper and copper salts had been studied by Nilsson et al.²⁶ who interrupted partially complete decarboxylations of copper(I) phthalate and analysed the products formed (Scheme 7). Nilsson's results



Scheme 7

implicated one-electron transfer reactions of the carboxylate anions and the generation of free radical intermediates (or their covalently bonded copper equivalents) and showed that transient carbocations were unlikely.

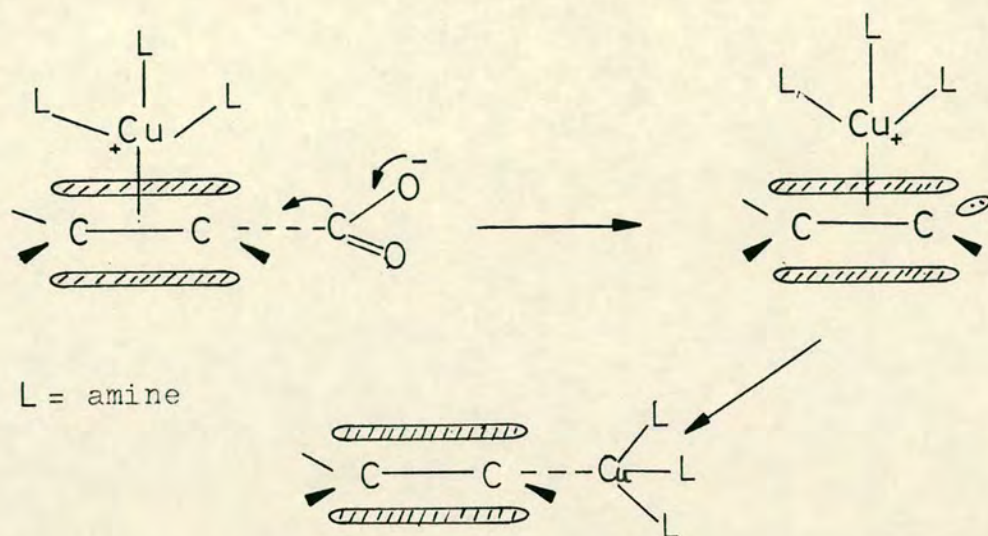
In view of Nilsson's work Paquette²⁴ anticipated, for an aliphatic acid, that interaction of Cu(I) with dianion (20) might lead via (21) to alkyl radical (22), the further redox reaction of which with Cu(I) would deliver the olefin, as outlined in Scheme 8.



Scheme 8

In order to increase the rate of this reaction Paquette added 2,2'-dipyridyl in equimolar quantities to the copper catalyst. The effect of this amine has been examined by Cohen and Schambach²⁸ who postulated that it promotes the reaction by stabilising the negative charge on the π -bonded cuprous ion which develops as carbon dioxide is lost and/or by increasing the electron withdrawing ability of the cuprous ion. Cohen

and Schambach's visualisation is shown in Scheme 9. This

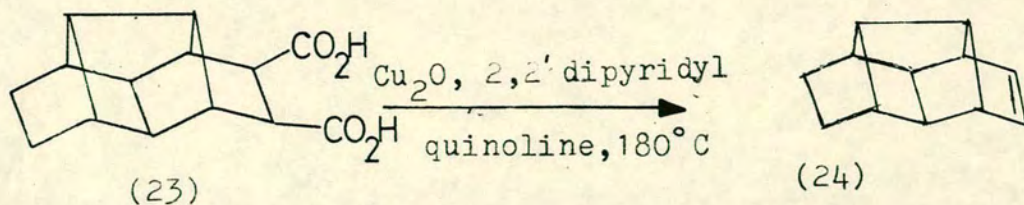


Scheme 9

work shows a greater than 94% retention of configuration of products and therefore rules out homolytic carbon-carbon bond cleavage. The postulated mechanism involves electrophilic attack of the cuprous ion at the carbon atom bearing the carboxyl group only if the subsequent loss of carbon dioxide is much faster than rotation about the resulting carbon-carbon bond.

Paquette's method of oxidative bis-decarboxylation involved heating a diacid with red cuprous oxide and 2,2'-dipyridyl in a solution of pyridine at ca. 180°C. Several diacids were successfully bis-decarboxylated and a comparison of the yields obtained for the conversion of the 2-norbornyl system (23) into the strained alkene (24) with conventional methods is given in Scheme 10.

One drawback to this procedure is the need for high temperatures to effect bis-decarboxylation and subsequent retro-Diels-Alder fragmentations which occur under these forcing



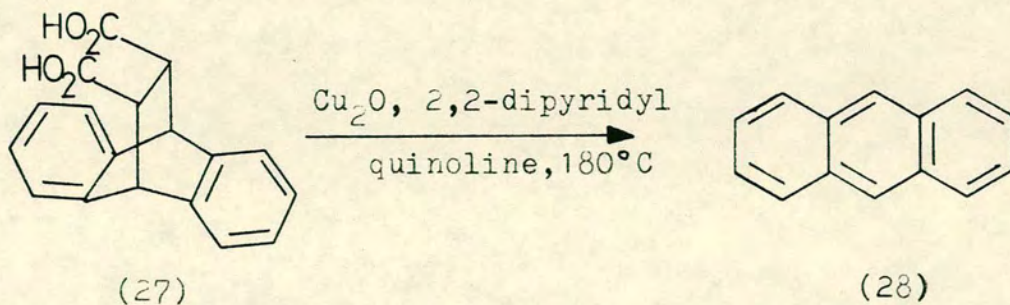
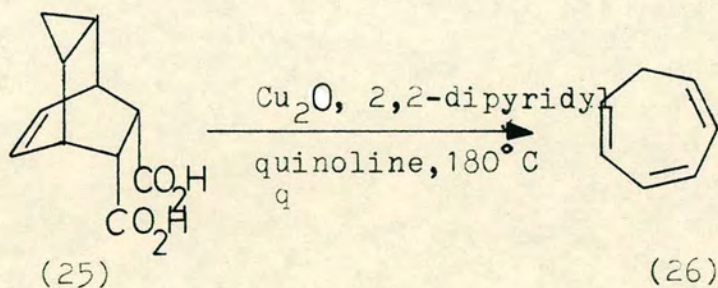
Copper salt 42%

$\text{Pb}(\text{OAc})_4$ 0%

Electrolysis 20 -27%

Scheme 10

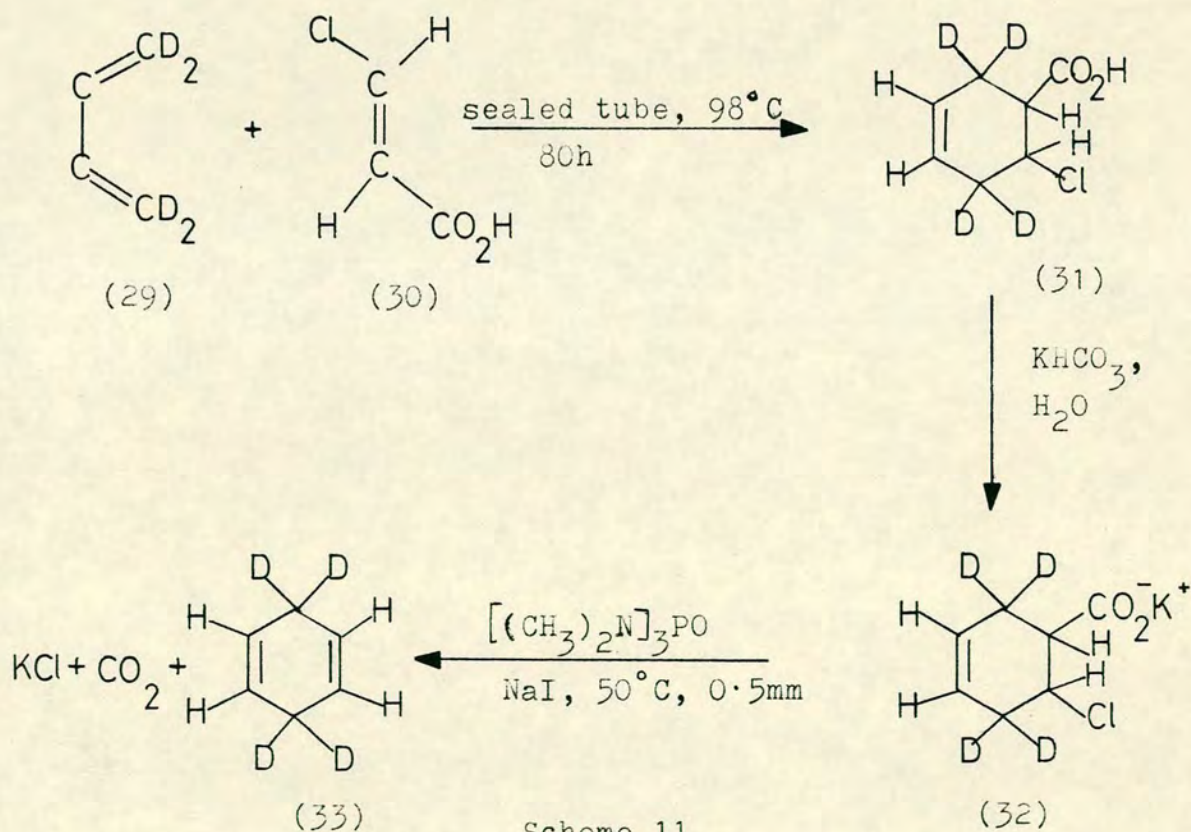
conditions. Two such examples of this fragmentation have been reported by Paquette, viz. treatment of (25) and (27) to give cycloheptatriene (26) and anthracene (28), respectively.



Alternatives to maleic anhydride as an acetylene equivalent

a. trans- β -Chloroacrylic acid

In 1968 Norris,²⁹ searching for a route to 3,3,6,6-d₄-cyclohexa-1,4-diene (33), reacted the readily available 1,1,4,4-d₄-buta-1,3-diene (29) with trans- β -chloroacrylic acid (30) to give the carboxylic acid (31) which was subsequently converted into the potassium salt (32). Decarboxylation of the potassium salt (32) with tris(dimethylamino)phosphine oxide gave the desired product (33) in 45% overall yield.



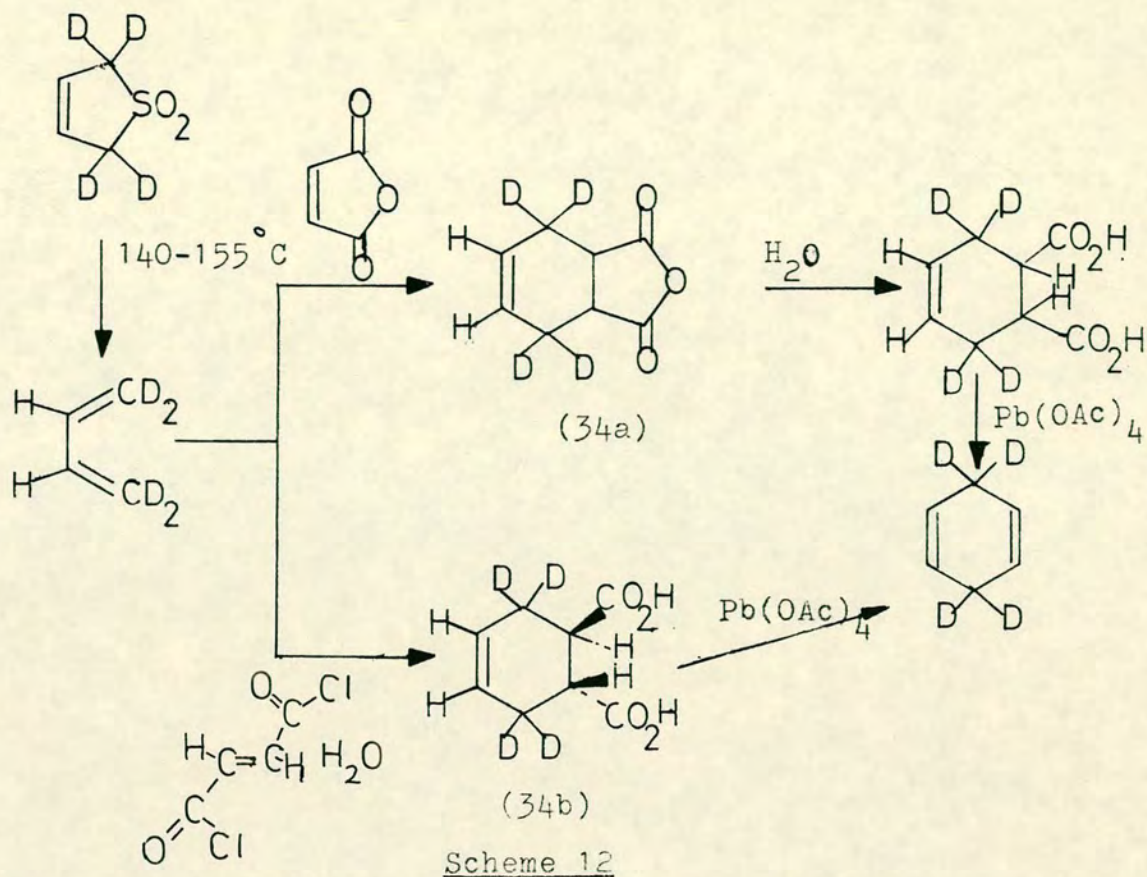
Scheme 11

In the overall strategy of this route, β -chloroacrylic acid serves as a novel acetylene equivalent. Although this procedure incorporates three steps, the product can be distilled off as fast as it is generated thus eliminating any disproportionation or oxidation. Interestingly, it was observed that

only the trans-isomer underwent elimination³⁰ leaving the cis-isomer unreacted. However, if sodium iodide was added to the reaction the cis-isomer did react. Presumably, the iodide ion displaces the chloride of the cis-isomer thus giving a trans-iodo-isomer which can then eliminate iodide and carbon dioxide.

b. Fumaroyl chloride

Wolfe and Campbell³¹ have recently introduced fumaroyl chloride as an alternative dienophile to maleic anhydride in the reaction with 1,3-butadienes, leading to selectively deuteriated cyclohexenes and 3,3,6,6-d₄-cyclohexa-1,4-diene by subsequent treatment with lead tetraacetate. Compared to the foregoing method of Norris fumaroyl chloride reacted with 1,3-butadiene under much milder conditions. Moreover it was found that the maleic anhydride adduct (Scheme 12) (34a) gave cis-diacids upon hydrolysis whereas fumaroyl chloride afforded trans-diacids (34b). Subsequent bis-decarboxylation by lead tetraacetate showed that the trans-diacid reacted without deuterium scrambling whilst the corresponding reactions with the cis-diacid led to significant scrambling. It was argued on the basis of these results that stereoelectronic effects operated in the bis-decarboxylation of cyclohexene- and cyclohexane-1,2-dicarboxylic acids. These conclusions conflict with the work of Corey³² and others³³ who claim that there is no such stereoelectronic control.



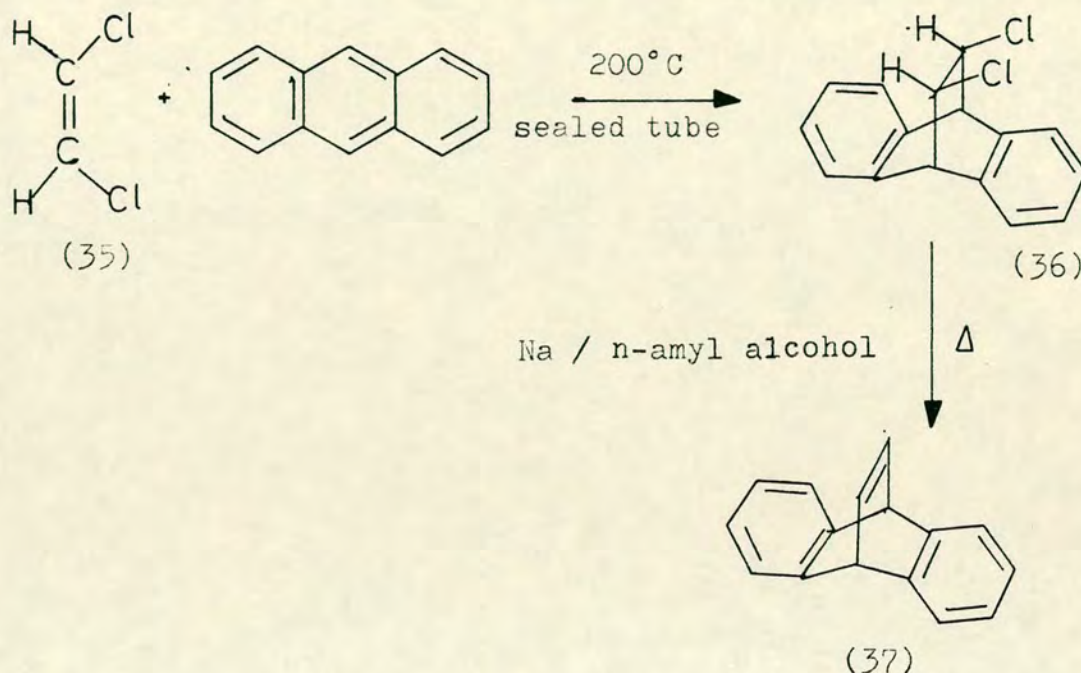
In view of the lack of deuterium scrambling in the bis-decarboxylation of trans-diacids it can be concluded that fumaroyl chloride is superior to maleic anhydride as an acetylene equivalent for the Diels-Alder synthesis of specifically deuteriated cyclohexenes.

3. Alternative acetylene equivalents precluding the need for oxidative decarboxylation

a. cis-1,2-Dichloroethylene

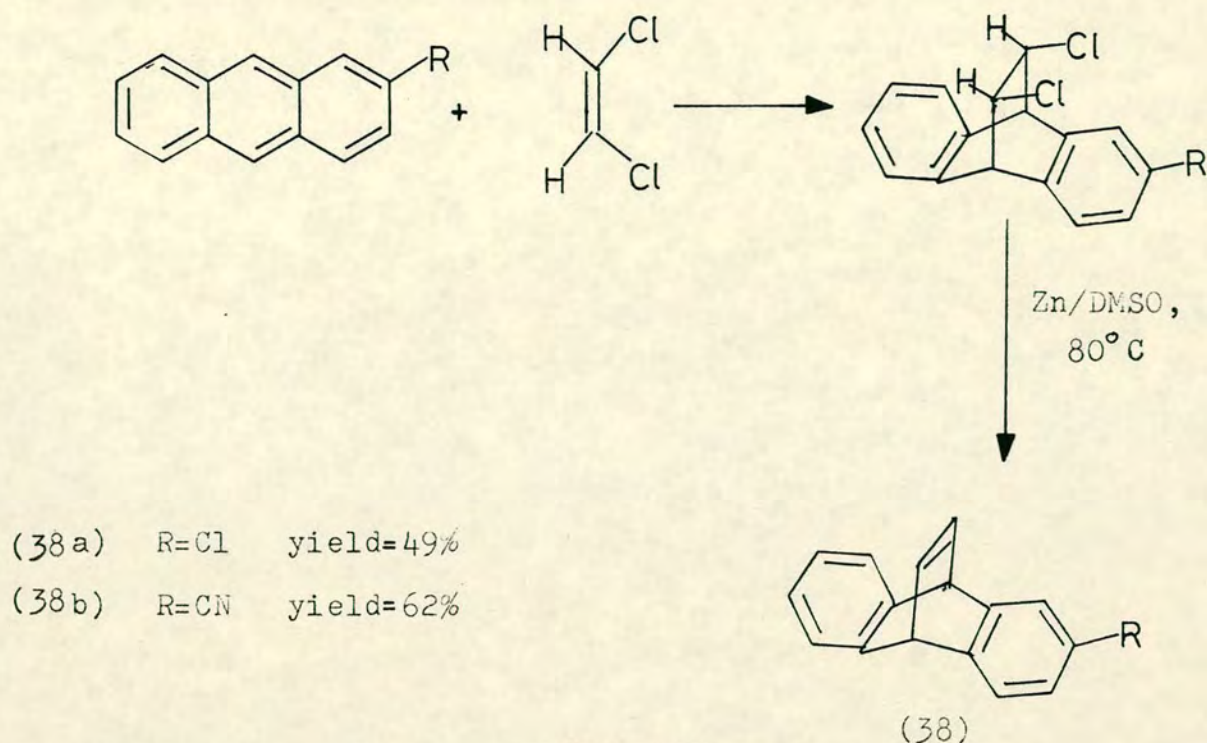
An acetylene equivalent which precludes the need for oxidative decarboxylation in the final step of the synthesis was first reported in 1952 by Cristol et al.^{34,35} who reacted

trans- or cis-1,2-dichloroethylene (35) with anthracene at 200°C to give the adduct (36). Subsequent dechlorination of the latter was effected with sodium in n-amyl alcohol³⁵ at reflux temperature to give dibenzobarrelene (37) in 56% yield.



In an effort to find new routes leading to substituted dibenzobarrelenes Figeys and Dralants⁴ applied Cristol's method to 2-substituted anthracenes. Unfortunately, the conditions for dechlorination proved to be too drastic for most of the adducts obtained. However, modification of the dechlorination procedure by using a dipolar aprotic solvent eg. dimethyl sulphoxide³⁶ instead of an alcohol, allowed the 2-cyano (38b) and 2-chloro (38a) dibenzobarrelenes to be formed in high yields as shown in Scheme 13.

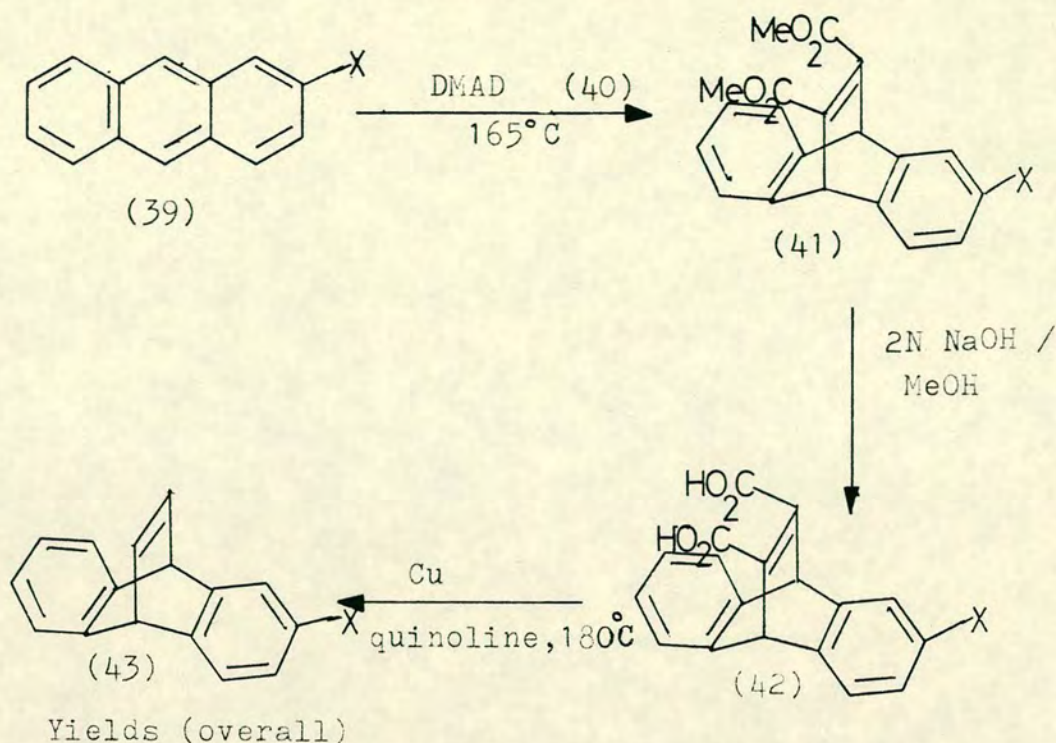
In the course of this work, Figeys and Dralants utilised another acetylene equivalent in the form of dimethyl acetylene dicarboxylate to give a higher yielding synthesis of dibenzobarrelene and 2-chlorodibenzobarrelene.



Scheme 13

b. Dimethyl acetylene dicarboxylate

Dimethyl acetylene dicarboxylate (DMAD) (40) has been used as a dienophile for many years. Indeed Diels and Alder first reported³⁷ the reaction of DMAD with anthracene as long ago as 1931. It is a substituted acetylene which is made more reactive towards dienes, by virtue of the electron withdrawing effect of the two ester groups. Figeys and Dralants⁴ have used DMAD according to the simple procedure shown in Scheme 14 to prepare dibenzobarrelenes (43a) and (43b). The addition of DMAD to the anthracenes (39a) and (39b) proceeded readily in high yields and was followed by the quantitative conversion of the dimethyl esters (41a) and (41b) into the corresponding diacids (42a) and (42b). The subsequent reductive decarboxylation of the diacids was accomplished with copper powder in quinoline at 180°C.



(43a) Cl = 22%

(43b) H. = 71%

Scheme 14

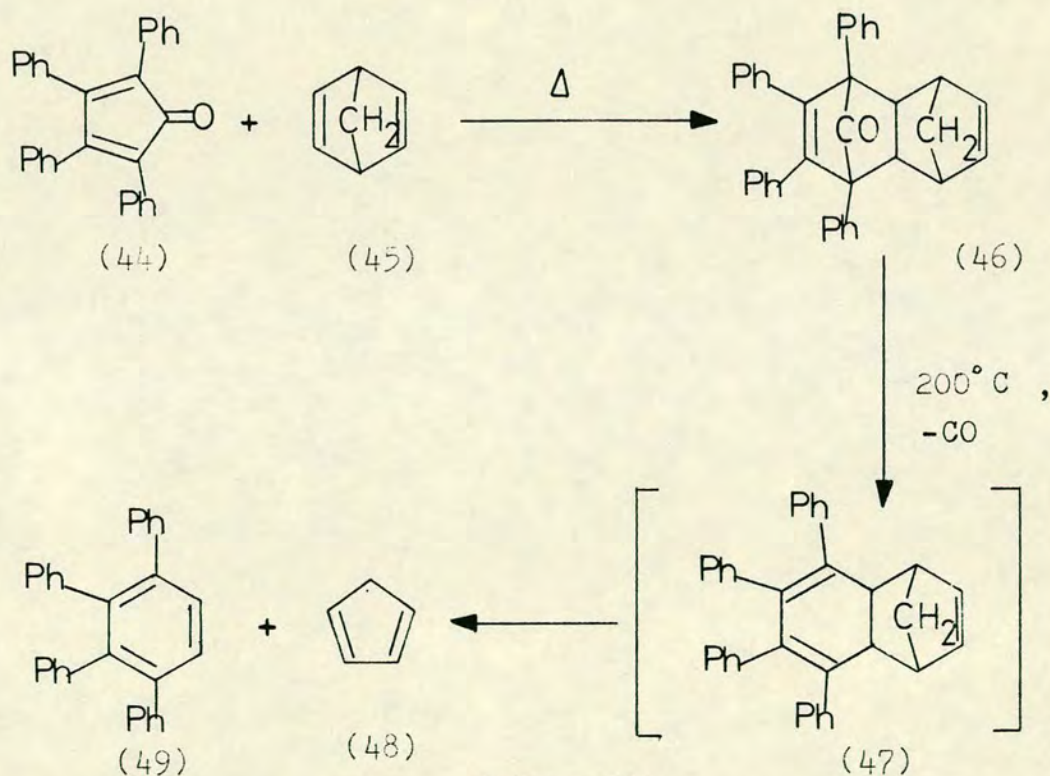
The use of this method gave dibenzobarrelene (43b) in an overall yield of 71% which compared favourably to the slightly modified method of Cristol (see Scheme 13), which gave a yield of 56%. As in the preparation using dichloroethylene, high temperatures are necessary to carry out the initial additive step which precludes the use of thermally sensitive starting materials. Isolation of anthracene as one of the final products also pointed to an unwanted retro-Diels-Alder reaction operating in the final copper-catalysed reduction step.

c. Retro-Diels-Alder reaction involving the loss of cyclopentadiene

In all the procedures discussed so far the occurrence of a retro-Diels-Alder reaction in the final step has been detrimental in the overall strategy. Indeed the regularity of its occurrence has prompted workers to devise procedures involving

acetylene equivalents whose mode of action depends upon the thermal extrusion of a stable moiety from an adduct.

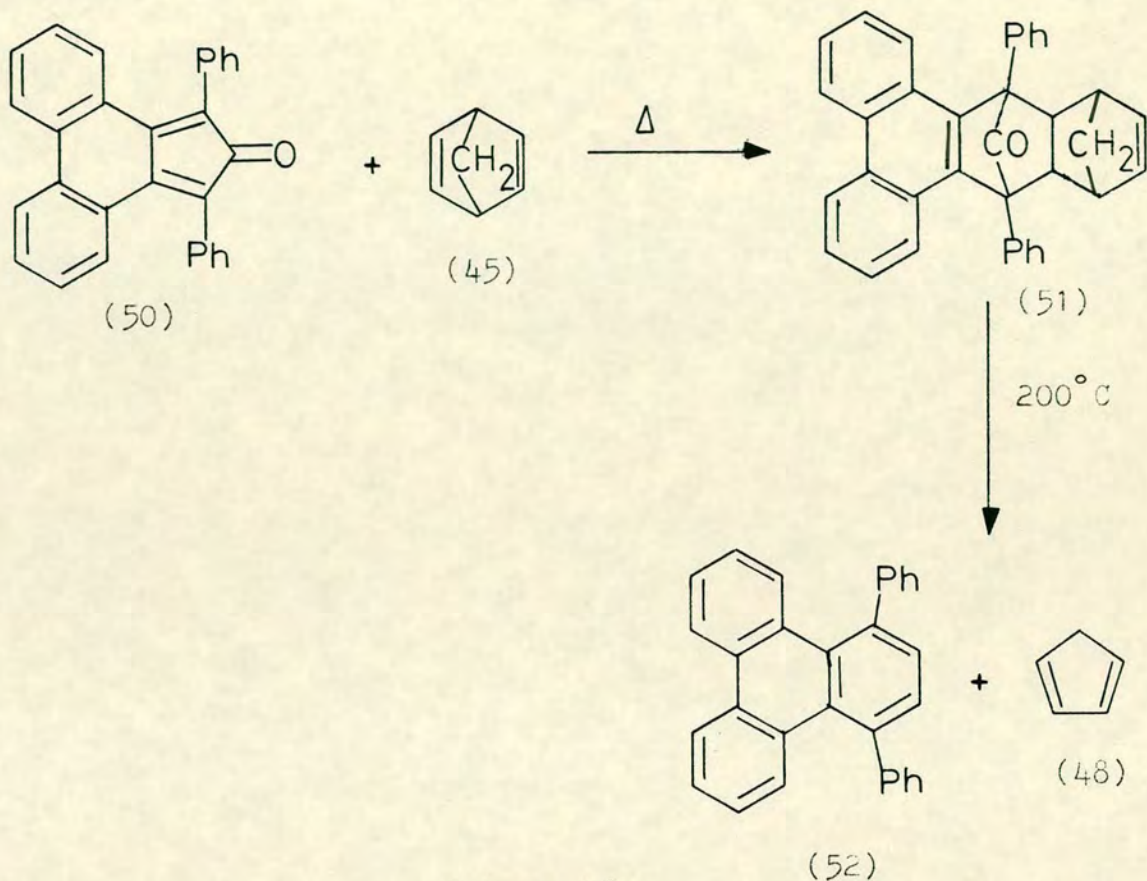
The first report to utilise this approach was by Mackenzie³⁸ who prepared a variety of tetra-substituted benzenes by a one-pot reaction of norbornadiene (45) with substituted cyclopentadienones (44). Heating of the adducts (46) at temperatures in excess of 200°C resulted in the concomitant loss of cyclopentadiene (48) and carbon monoxide to give the desired product (eg.49) in 92% overall yield. Scheme 15 shows the reaction



Scheme 15

scheme formulated by Mackenzie who presumed that compounds (46) and (47) were formed, albeit fleetingly, under the reaction conditions since only tetraphenyl benzene and cyclopentadiene were isolated. In another typical example where norbornadiene serves as an acetylene equivalent, 1,4-diphenyltriphenylene (52) has been prepared in 85% overall yield as shown in Scheme 16.

Thus norbornadiene (45) was reacted with phencyclone (50) to give the isolable adduct (51), thermolysis of which gave 1,4-diphenyltriphenylene (52).

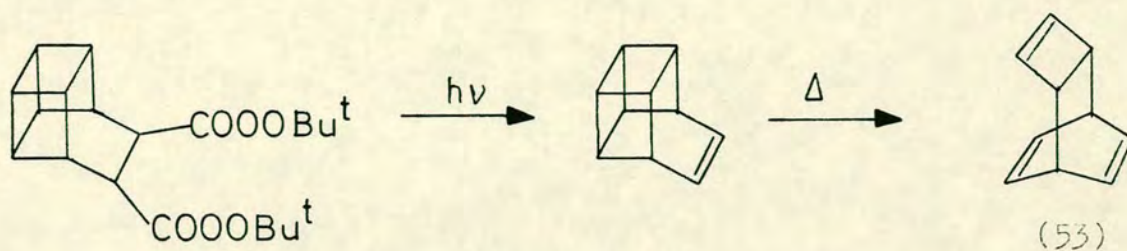


Scheme 16

d. Decomposition of peresters

Masamune et al.³⁹ has reported an alternative synthesis of a cyclic alkene from a vicinal dicarboxylic acid via decomposition of its perester, either thermally or photochemically, the latter process being particularly suitable for the preparation of highly strained alkenes. The preferred method involved conversion of a dicarboxylic acid into its acid chloride followed by treatment with t-butylhydroperoxide⁴⁰ to give the corresponding di-t-butylperester. Scheme 17 illustrates the method for the synthesis of Nenitzsecu's hydrocarbon (53). The yields obtained

were similar irrespective of whether the reaction was carried



Scheme 17

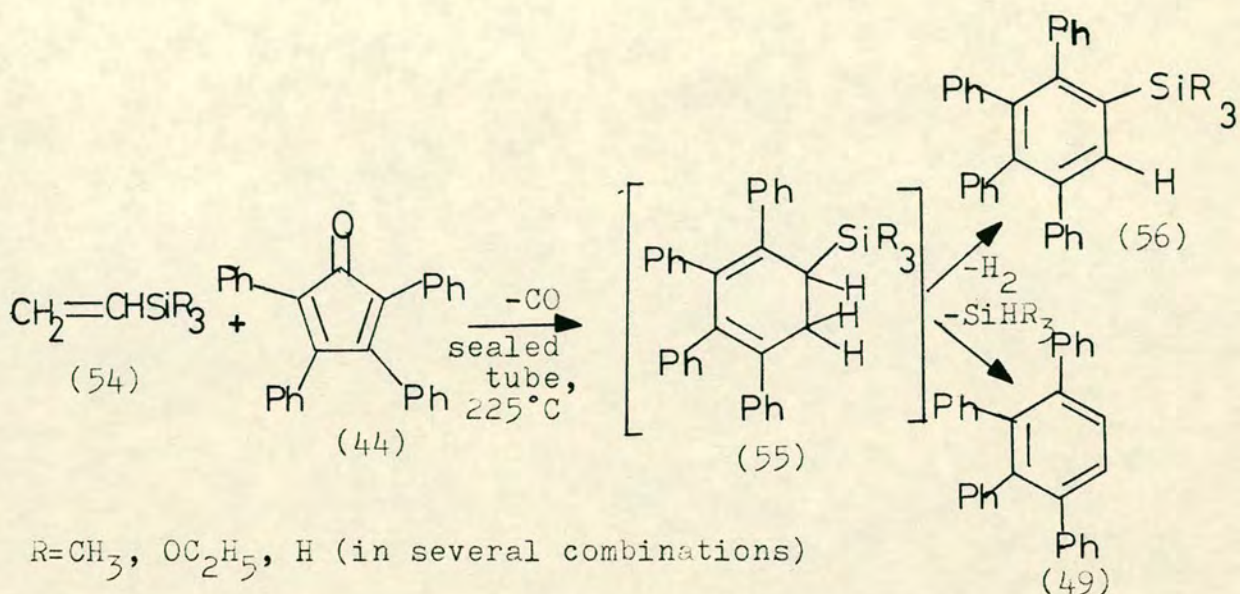
out under photochemical or thermal conditions. To date this procedure has not been applied extensively and its general utility is unknown.

4. Acetylene equivalents developed since 1970

a. Vinyl Silanes

Organosilicon compounds possessing unsaturation adjacent to the heteroatom have been investigated as potential acetylene equivalents by Freeburger and Spialter.⁴¹ Their investigations utilised tetraphenylcyclopentadienone (44) exclusively as the diene and the reader is referred to their publication for information concerning the general nature of the acetylene equivalents, their advantages and disadvantages. In a typical reaction, condensation of the vinyl silane (54) with (44) gives rise to a mixture of tetraphenylbenzene (49) and the tetraphenylsilane (56) in varying amounts depending upon the reaction conditions. This is due to the fact that the intermediate dihydrobenzene (55) can aromatise in two ways, either by loss of hydrogen to produce the phenylsilane (56) or by the loss of

the silane fragment to produce 1,2,3,4-tetraphenylbenzene (49). With vinyl trimethylsilane as the dienophile it was found that

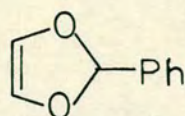


only aromatic solvents gave detectable amounts of the tetraphenylsilane (56) and as the amount of ethoxy groups on the silicon increased so did the amount of silicon-containing product. The solvent effect is difficult to rationalise but the increase in number of electronegative groups on the silicon is thought to strengthen the Si-C bond thus causing more of (56) to be formed.

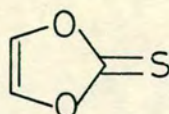
Although the vinyl silane (54) acts as an acetylene equivalent with (44) under forcing conditions it is not a practical synthon due to the unpredictability of the aromatisation step. However, it should be noted that the authors were interested in the formation of the tetraphenylsilane (56) and not in the use of the vinyl silanes as acetylene equivalents.

b. 2-Phenyl- and 2-thiono-1,3-dioxol-4-ene

Anderson et al.⁴² have reported the use of 2-phenyl- and 2-thiono-1,3-dioxol-4-enes, (57) and (58) respectively, as acetylene equivalents. Their approach involved treatment of

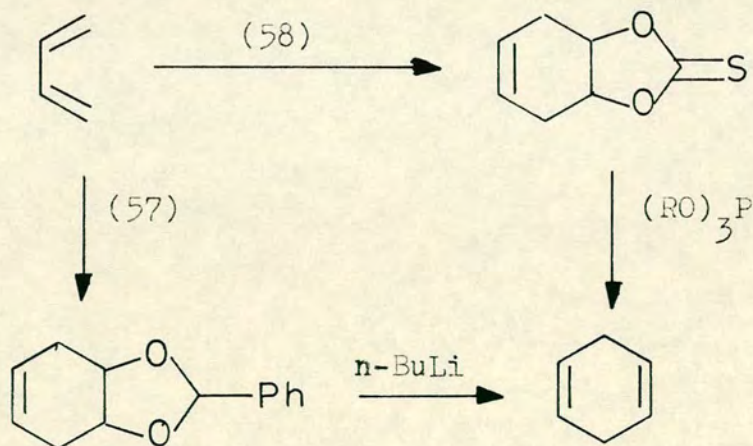


(57)



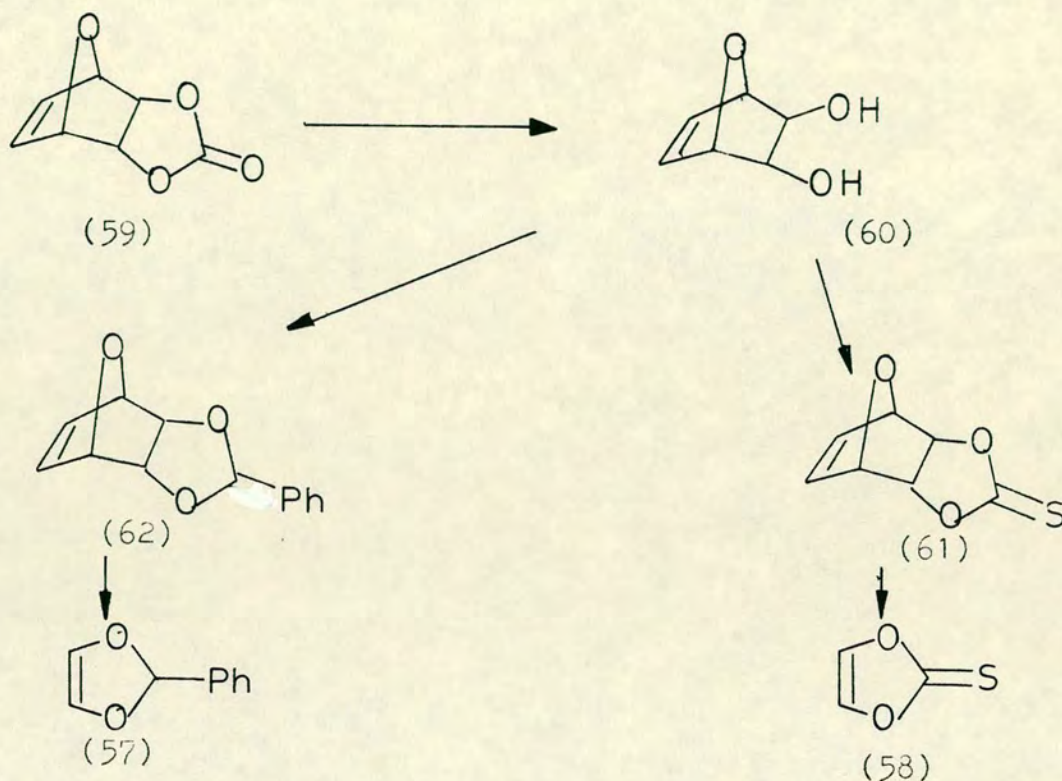
(58)

diene-derived adducts with either trivalent phosphones or *n*-butyllithium to form the corresponding olefin as shown in Scheme 18.

Scheme 18

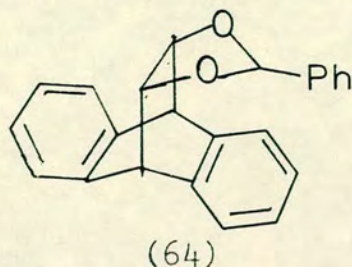
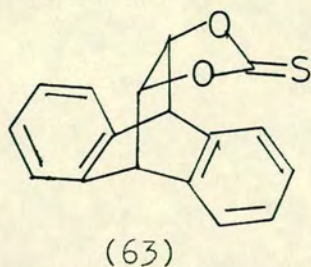
The method of formation of the dienophiles (57) and (58) involved the formation of the cyclic carbonate (59) by the Diels-Alder reaction between vinylene carbonate and furan. The carbonate (59) was then hydrolysed to the diol (60) which was converted into (61) by treatment with N,N-thionocarbonyl

diimidazole in toluene. Thermolysis of (61) at 160°C extracted furan to afford (58) in an almost quantitative yield.

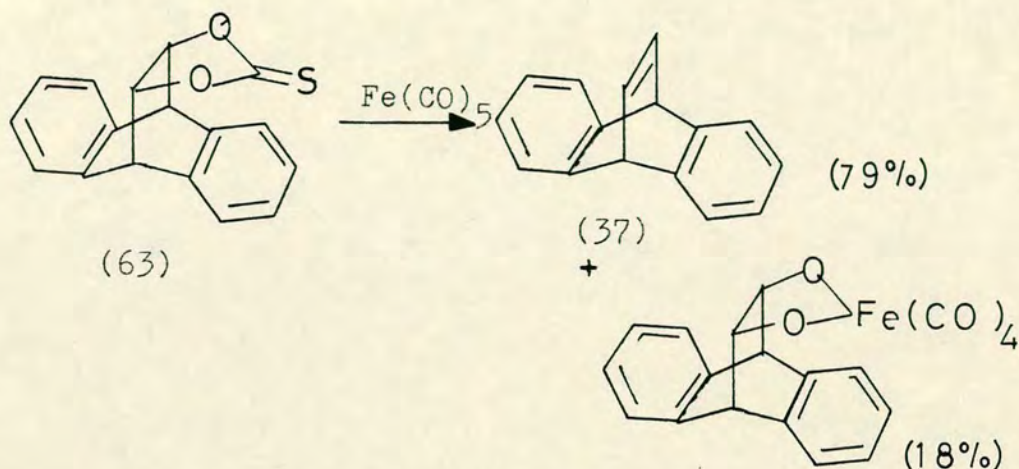


The corresponding reaction of the diol (60) with benzaldehyde gave rise to (62) in 95% yield, thermolysis of which at 170°C led to loss of furan and the formation of the unstable 2-phenyl-1,3-dioxol-4-ene (57) in 15% yield.

Vinylene thionocarbonate (58) and 2-phenyl-1,3-dioxol-4-ene (57), generated in situ from (62) were each reacted with anthracene in benzene at 170°C for 16 h to give the adducts (63)



and (64). Further work by Daub *et al.*⁴³ involved the treatment of the former with $\text{Fe}(\text{CO})_5$ which resulted in the formation of dibenzobarrelene in 79% yield (Scheme 19).

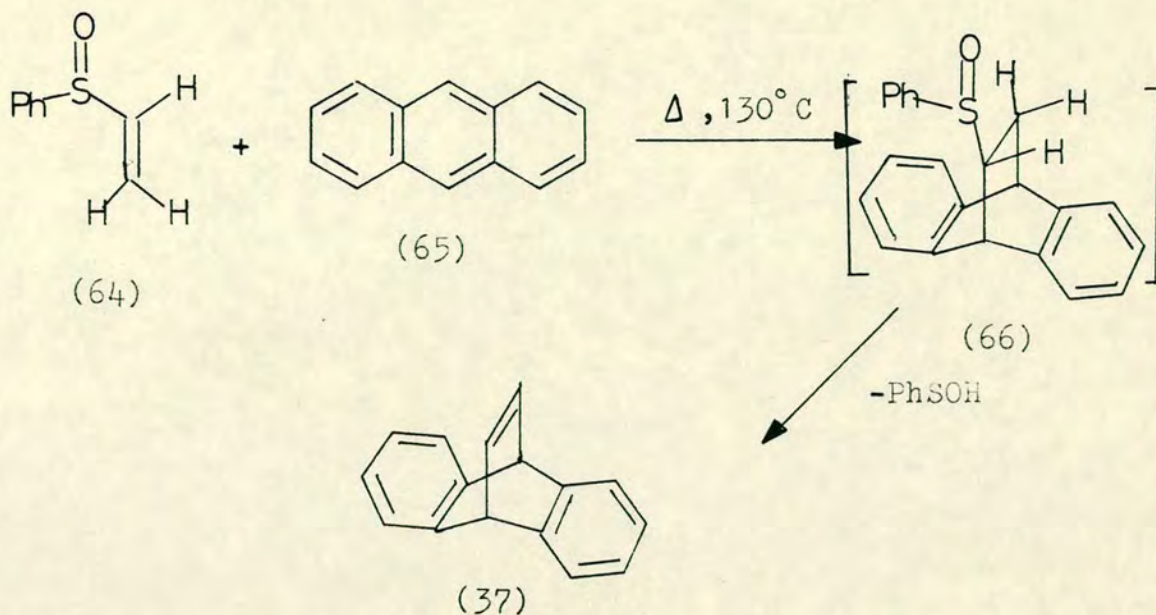


Scheme 19

c. Phenyl vinyl sulphoxide

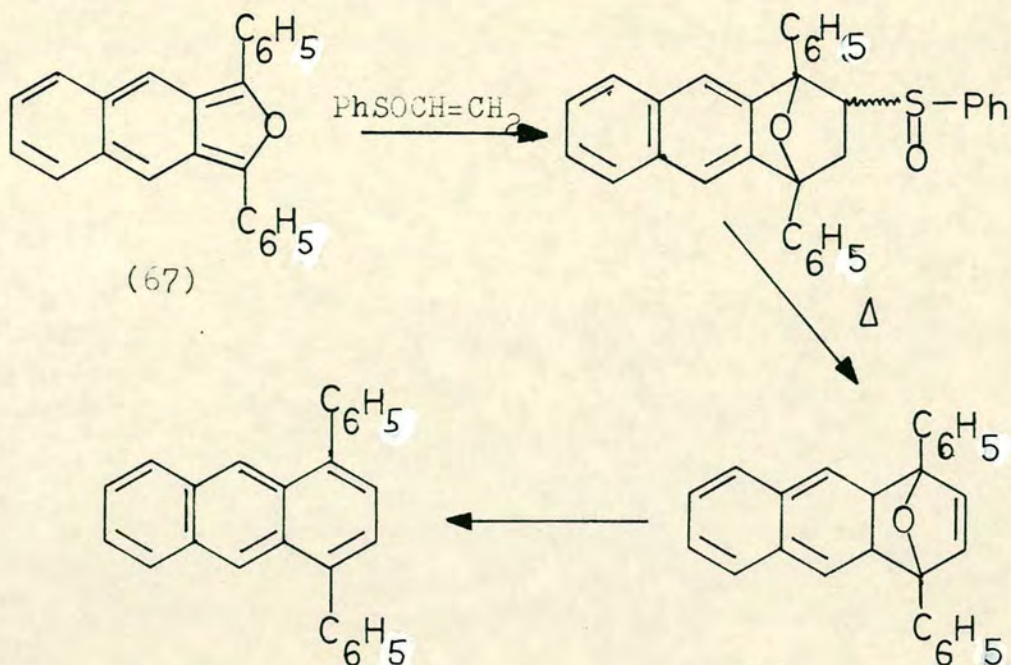
In 1978 Paquette *et al.*⁴⁴ reported the use of phenyl vinyl sulphoxide (64) as an alternative to all previous acetylene equivalents.* The reagent, easily prepared by the reaction of ethyl phenyl sulphinate with vinyl magnesium bromide, derives its usefulness from the fact that the presence of the sulphoxide group enhances the dienophilicity of the double bond considerably, thus allowing reaction with many dienes. Scheme 20 illustrates this one-pot procedure in which two steps occur simultaneously for the reaction of sulphoxide (64) with anthracene, to give dibenzobarrelene by loss of phenylsulphenic acid from the adduct (66).

* This synthon had been previously mentioned in the literature⁴⁵ but probably because of claims of low reactivity, it had not received previous attention.



Scheme 20

The usefulness of this acetylene equivalent is based upon the idea that the cycloaddition could be effectively driven to completion before thermal decomposition of the sulphoxide (64) occurred. In practice the sulphoxide proved to be much more reactive than thermally labile, as was observed in the aforementioned reaction with anthracene which gave dibenzobarrelene in an isolated yield of 83%. In similar reactions, other dienes such as tetraphenylcyclopentadienone, diphenylisobenzofuran and diphenyl-5-tetrazine in toluene gave greater than 90% yields of products. However, in the case of 1,3-diphenylisobenzofuran and 1,3-diphenylnaphtho[2,3-c]furan (67) the liberated phenylsulphenic acid appeared to be capable of deoxygenating the adduct; scheme 21 shows the reaction with the naphthofuran (67). This may be a useful side reaction since aromatisation of isobenzofuran adducts usually requires catalytic reduction of the double bond and subsequent treatment of hydrogen bromide in acetic anhydride ⁴⁶.



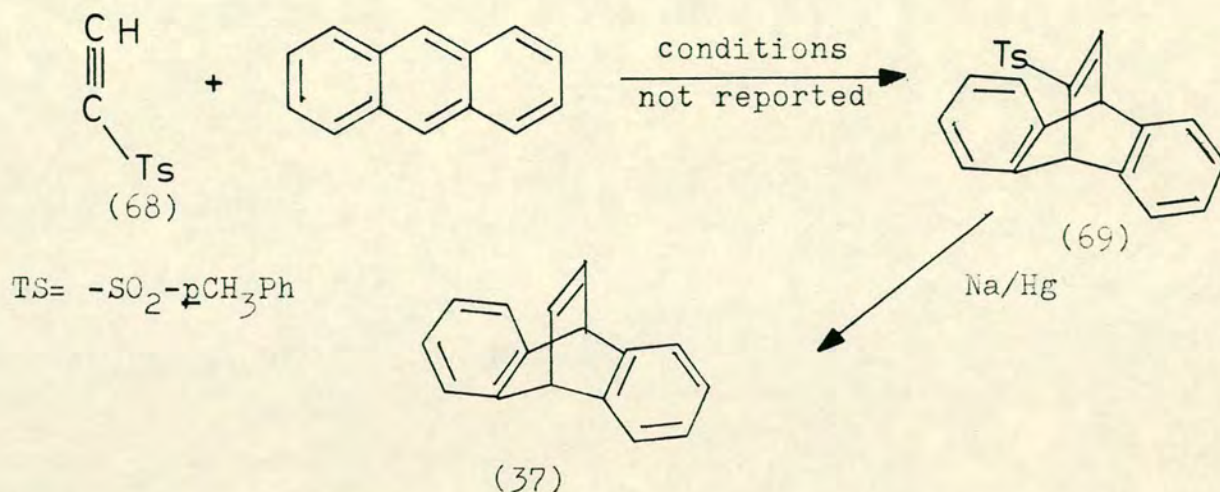
Scheme 21

In an extension of the work by Paquette's group Masumoto has reported a convenient preparation of 1,2 unsubstituted 3-cyanoindolizines which are key intermediates for the synthesis of [2.2.3]cyclazines⁴⁷⁻⁵⁰ by using phenylvinylsulphoxide as an acetylene equivalent with dicyanomethylides (see also Scheme 23).

d. Ethynyl p-tolyl sulphone

Following Paquette's work on the use of phenyl vinyl sulphoxide as an acetylene equivalent Davis⁵¹ reported an alternative approach involving the use of a substituted acetylene, $\text{XC}\equiv\text{CH}$, where X activates the triple bond towards reaction with dienes but is subsequently replaced by a hydrogen atom to give a non substituted product. This method utilised ethynyl p-tolylsulphone (68) which underwent cycloaddition with a variety of conjugated dienes such as cyclopentadiene, 1,4-diphenylbuta-1,3-diene and anthracene to give the respective adducts. In the case of anthracene, the sulphone (68) afforded

a 54% yield of the adduct (69) which in a reaction typical of

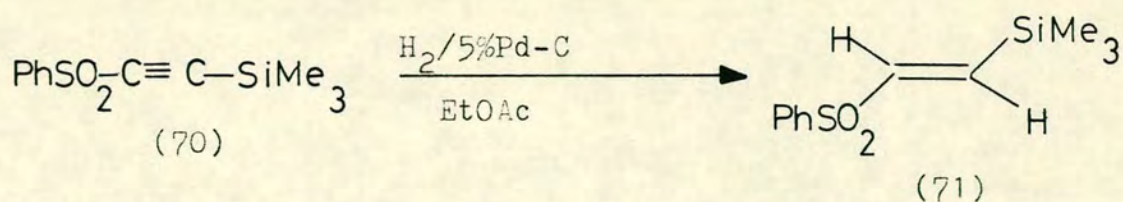


α,β -unsaturated sulphones^{52,53} could be reduced to dibenzo-barrelene in a 35% yield with sodium amalgam. It is worth noting that while (68) reacts under relatively mild conditions it requires a strong reducing agent to effect arylsulphonyl bond cleavage.

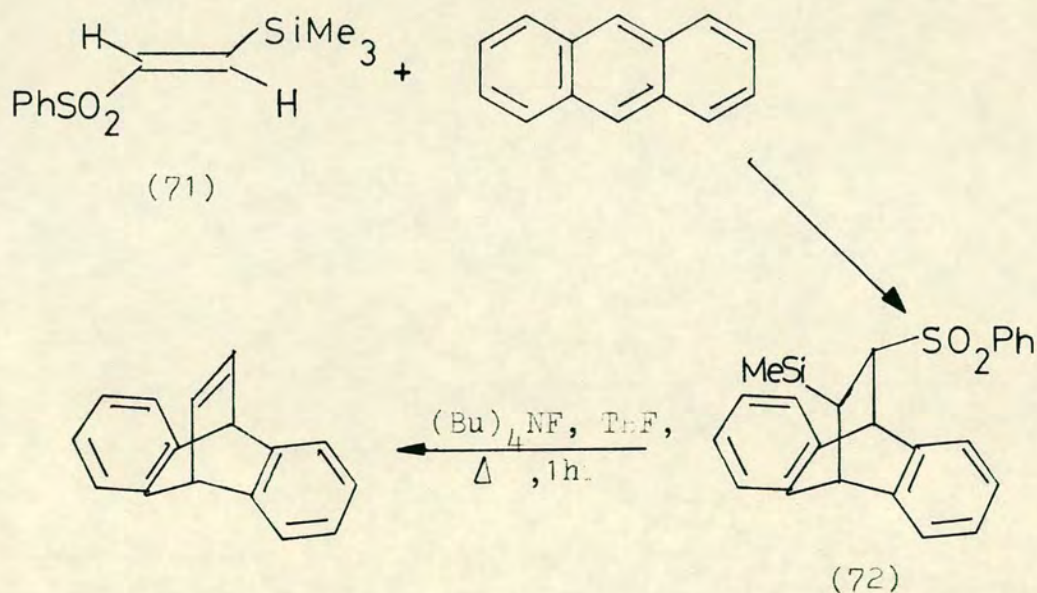
e. trans-1-Benzenesulphonyl-2-(trimethylsilyl)ethylene

In 1981 Paquette *et al.*⁵⁴ reported that trans-1-benzene sulphonyl-2-(trimethylsilyl)ethylene (71) could be used as an acetylene equivalent. Although the dienophilic reactivity of (71) was slightly lower than either ethynyl *p*-tolyl sulphone or phenylvinyl sulfoxide it served as a protocol for introducing $\text{RC}\equiv\text{CH}$ Diels-Alder equivalents and could be readily prepared in good yield by hydrogenation of the acetylene precursor (70) over a Pd/C catalyst.

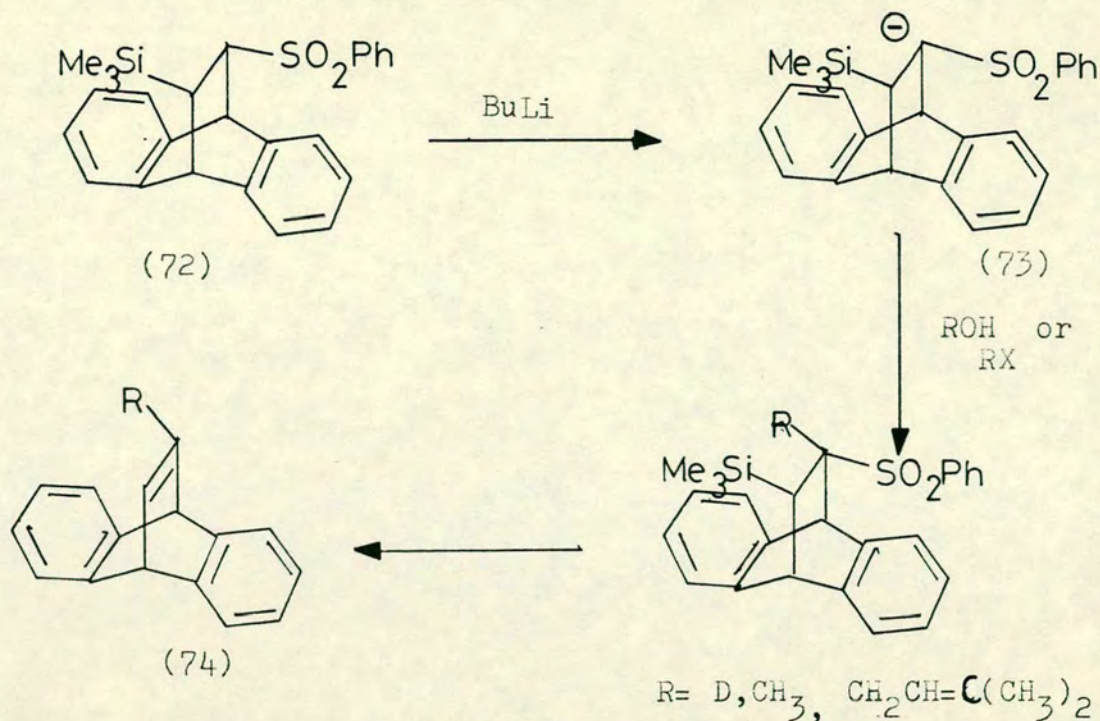
The reagent (71) successfully reacted with several dienes including anthracene which gave a 98% yield of the trans-adduct



(72) upon heating in a sealed tube at 160°C for 7 days. It is worth noting that the cis isomer needed to be heated for 2 weeks under the same conditions to give the same trans adduct in 35% yield, no evidence for the formation of the cis-product was found. Subsequent treatment of (72) with tetrabutylammonium fluoride in boiling THF gave dibenzobarrelene in 84% yield.



A key advantage of this method is that 2-substituted dibenzobarrelenes (74) can also be prepared from (72) via the formation of its α-sulphonyl carbanion (73) and subsequent quenching with various electrophiles as outlined in Scheme 22. However, as an acetylene equivalent which aims to place a carbon carbon double bond on a diene, trans-1-benzenesulphonyl-2-

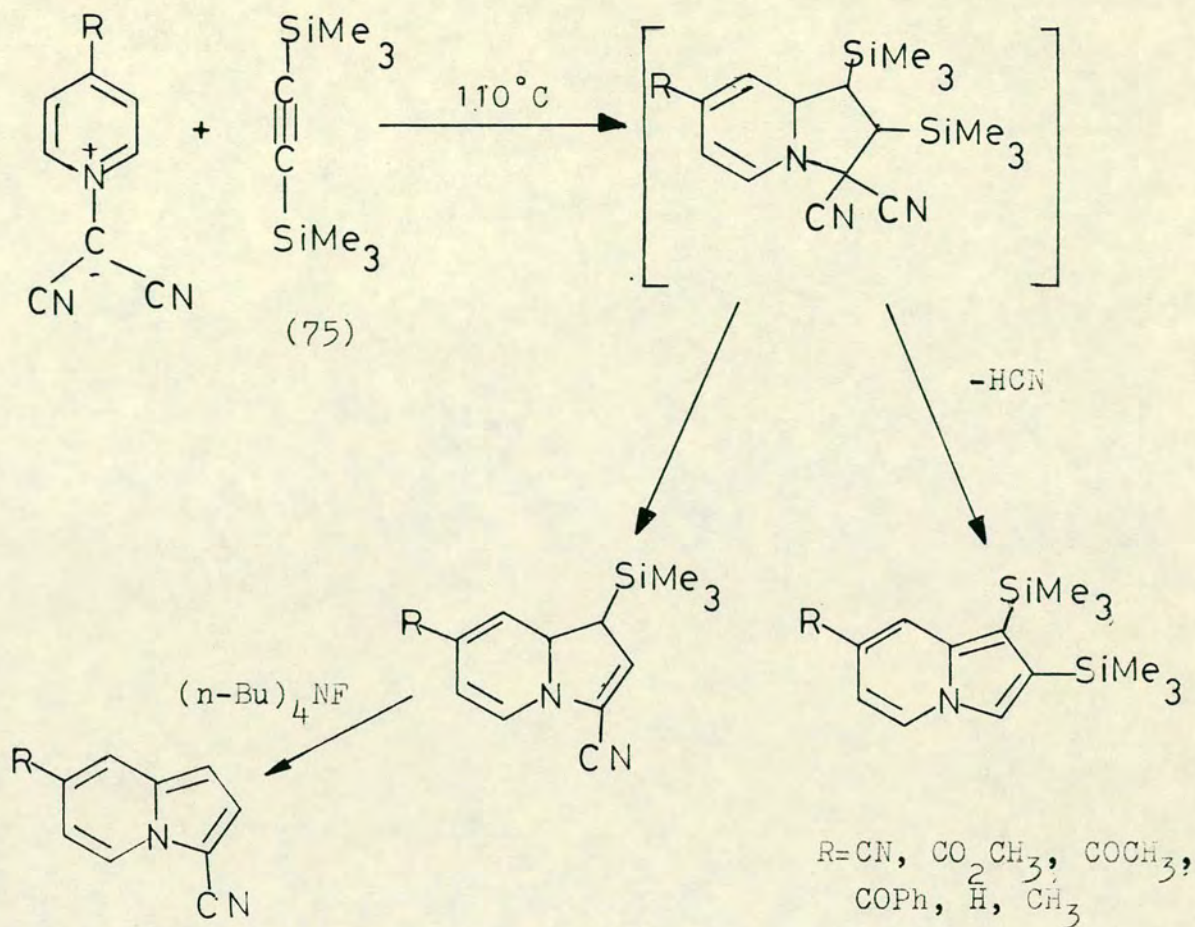


Scheme 22

(trimethylsilyl)ethylene (71) is less useful than phenyl vinyl sulphoxide, which needs less severe conditions to undergo the cycloaddition step. Nonetheless, because the alkene (71) allows the easy formation of alkyl substituted adducts it may prove to be more useful in certain cases.

f. Bis(trimethylsilyl)acetylene

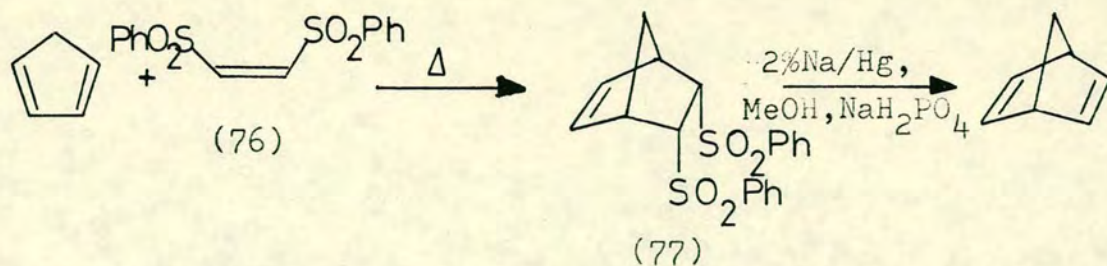
In a related approach Matsumoto *et al.* has employed bis²(trimethylsilyl)acetylene⁵⁵ (75) as an acetylene equivalent for the preparation of indolizines. These compounds were obtained in good to fair yields by reaction with dicyanomethylides as shown in Scheme 23.



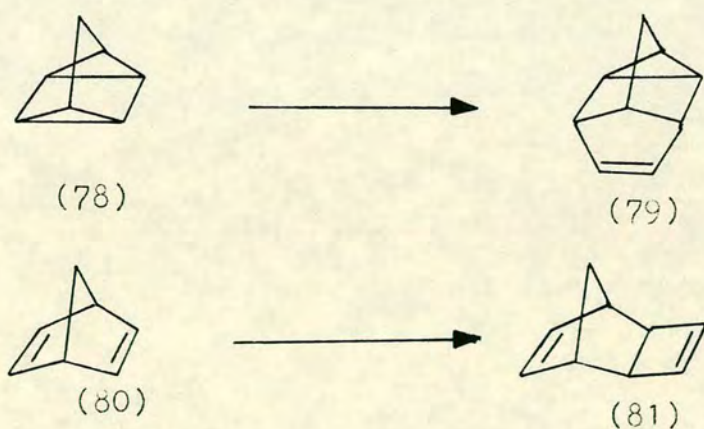
Scheme 23

g. 1,2-Bis(phenylsulphonyl)ethylene

The most recent work in the field of acetylene equivalents has been published by De Lucchi and Modena,⁵⁶⁻⁵⁸ who used cis-1,2-bis(phenylsulphonyl)ethylene (75) as a highly reactive dienophile. For example, their method of preparation of norbornadiene involved the addition of (76) to cyclopentadiene to form the adduct (77). Reduction elimination of the phenylsulphonyl group with 2% sodium amalgam then gave norbornadiene in 62% yield.

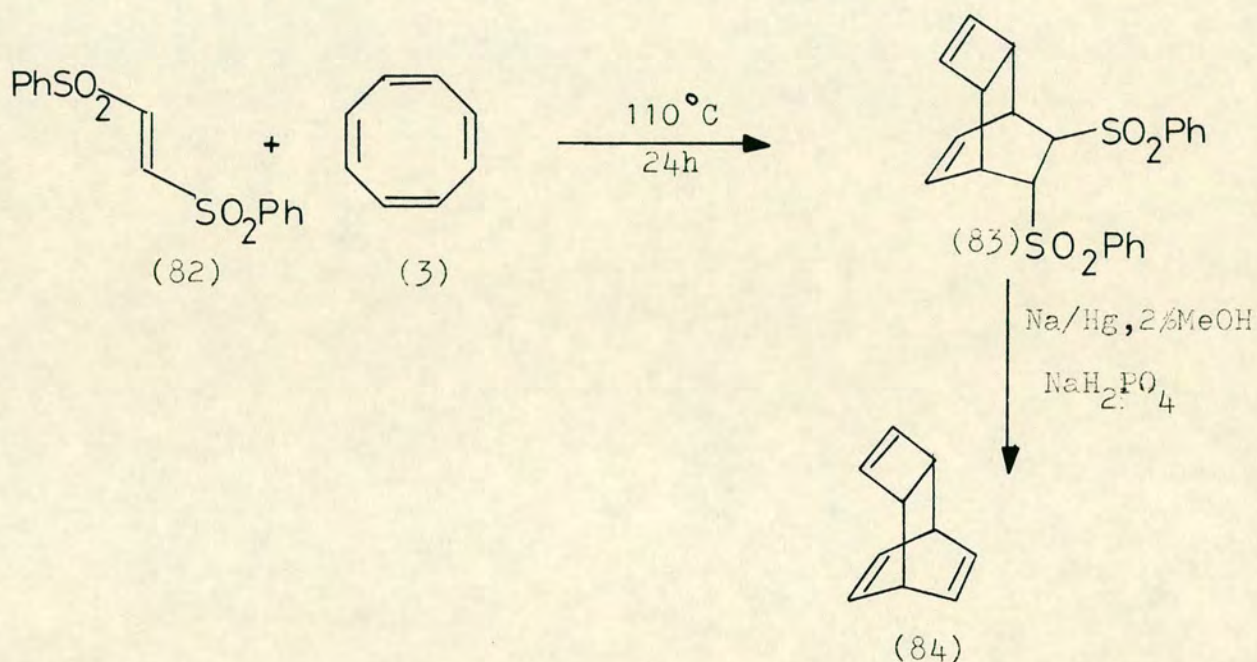


The enhanced reactivity of cis-1,2-bis(phenylsulphonyl)-ethylene (76) towards dienes in the Diels-Alder reaction is presumably due to the combined effects of two strongly electron-withdrawing sulphonyl groups. Because of the milder conditions required, the procedure has allowed the preparation of compounds containing strained σ bonds such as quadricyclone (79) from (78) and the cyclobutene (81) from norbornadiene (80) and hitherto represents the most convenient method for their synthesis.^{24,59,60} However, it was found that cis-1,2-bis(phenylsulphonyl)ethylene



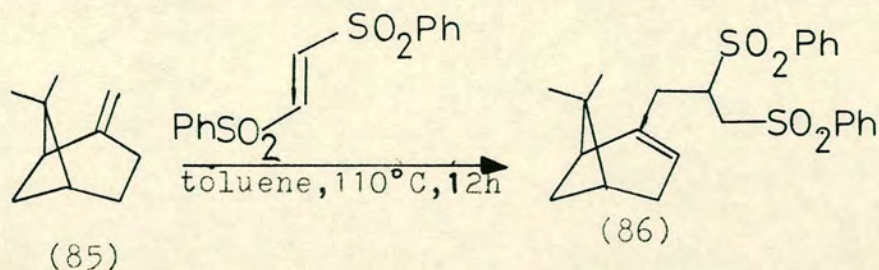
(76) did not add to less conventional dienes such as cycloheptatriene and cyclooctatetraene nor did its thermal instability allow for the use of more forcing conditions. In view of this instability De Lucchi and Modena⁶¹ focussed their attention upon the more stable trans-isomer (82) even though it was practically insoluble in toluene at room temperature. In the course of

their studies it was discovered that the trans-isomer was actually more reactive than the cis-isomer, this enhanced reactivity being ascribed to its greater thermal stability which allowed the use of higher reaction temperatures. For example the reaction of (82) with cyclooctatetraene (3) led to the formation of (83) which gave Nenitzescu's hydrocarbon (84) in an overall yield of 63% upon reduction with 2% sodium amalgam.



Scheme 24

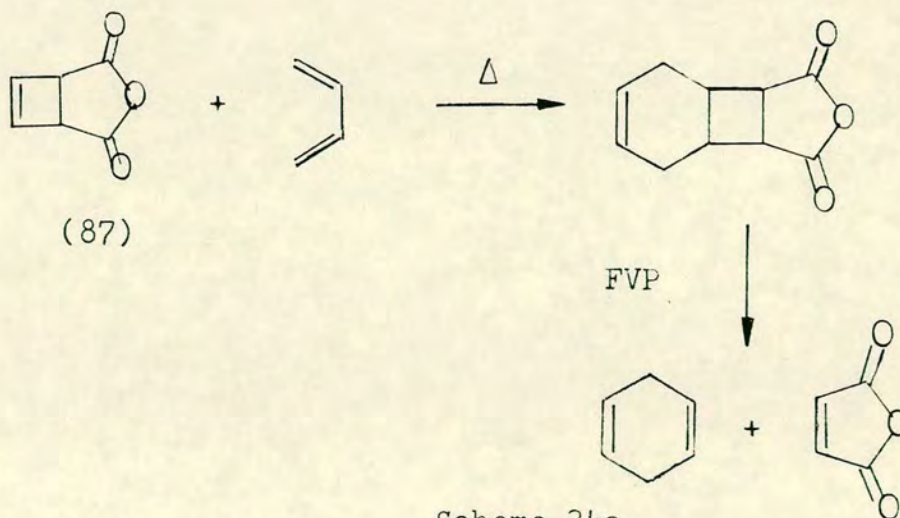
The trans-isomer (82) also reacted with β -pinene (85) to give the adduct (86) in 90% yield. This reaction is the first example of an acetylene equivalent which undergoes an 'ene' reaction.



In summary, trans-bis(phenylsulphonyl)ethylene (82) represents the most reactive acetylene equivalent prepared so far. However its use as an acetylene equivalent is marred by the need for a strong reducing agent for the removal of the phenyl sulphonyl groups in the final step. The method also requires the purification of the adduct prior to reduction thus lowering the overall yield. These factors must be taken into consideration when trans-bis(phenylsulphonyl)ethylene (82) is compared with the utility of phenylvinyl sulphoxide (64) for its facile one pot synthesis of alkenes.

B. Programme of Research

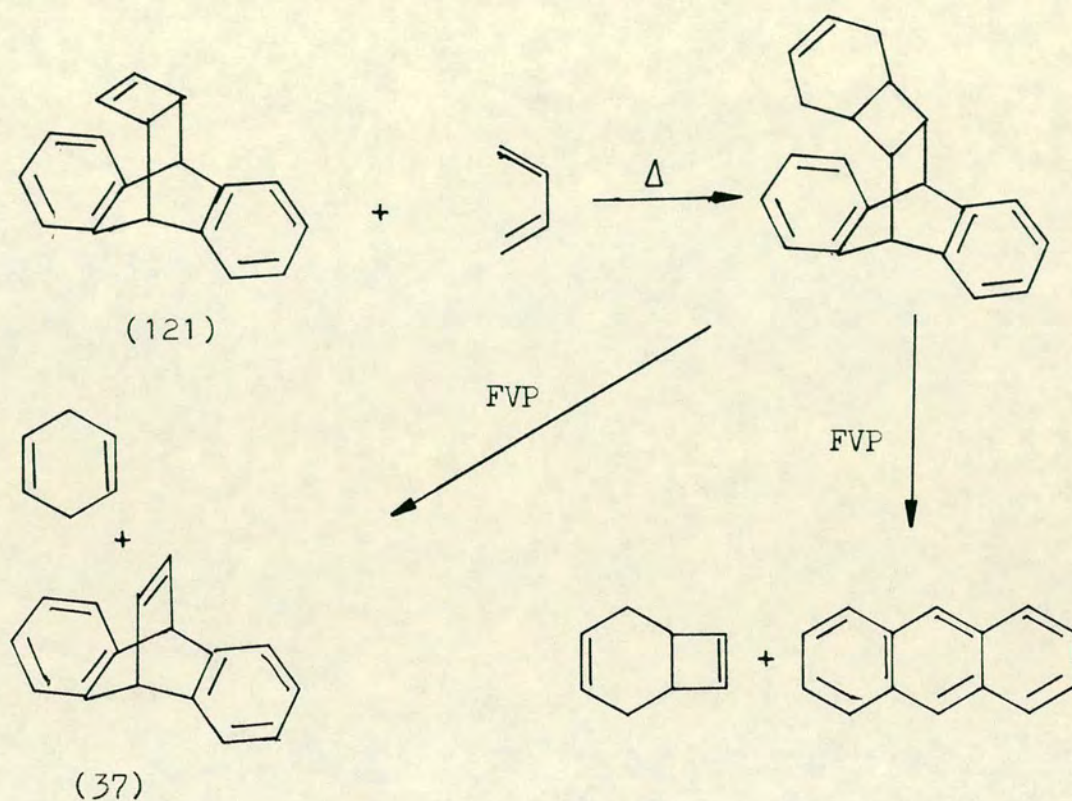
Cursory studies in these laboratories by Dr. E.J. Tinley showed that 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (87) formed cycloaddition products with various 1,3-dipolar and 1,3-diene reagents. When subjected to pyrolysis under flash vacuum pyrolytic conditions these adducts extruded maleic anhydride. A typical reaction is outlined in Scheme 24a, from which it can be seen that cleavage of maleic anhydride from the adduct results in the formation of a carbon-carbon double bond in the product. As a consequence the anhydride (87) functions as a dienophilic acetylene equivalent, a type of reagent that has aroused considerable recent interest. The initial aim of this work was to continue the investigation into the range of properties shown by (87).



Scheme 24a

The reaction of the anhydride (87) with anthracene led to the realisation that cyclobutananthracene (121) could be formed by a novel route. From Scheme 24b it could be seen

that this compound could serve either as an acetylene synthon by the loss of dibenzobarrelene (37) or, hopefully, as a cyclobutadiene synthon by extrusion of anthracene. The



Scheme 24b

ability of dibenzobarrelene to lose acetylene under FVP conditions¹³⁵ also prompted an interest in its ability to act as an acetylene synthon.

EXPERIMENTAL

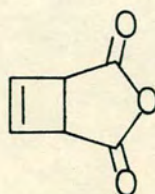
EXPERIMENTAL

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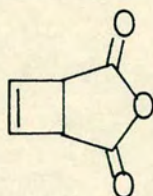
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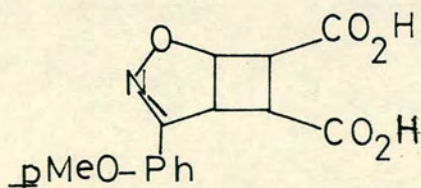
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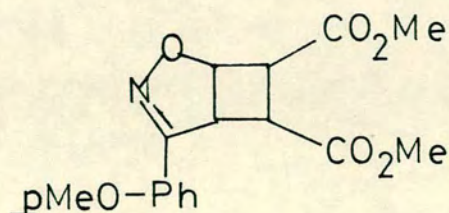
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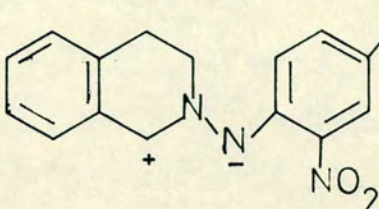


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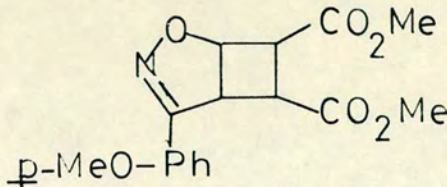
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f. Attempted reaction with $p - MeO-C_6H_4\overset{+}{C} \equiv N-\bar{S}$ 51

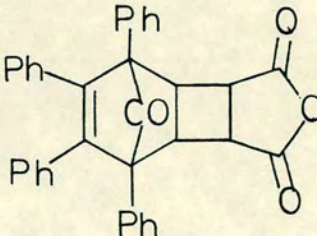
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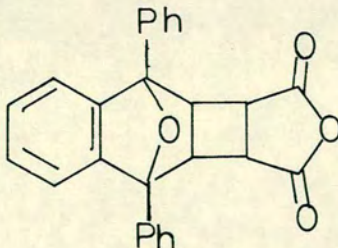
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a. FVP of  52

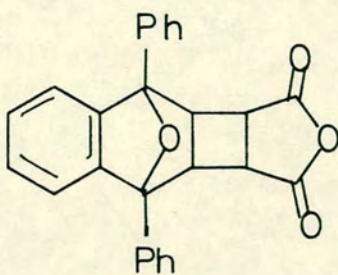
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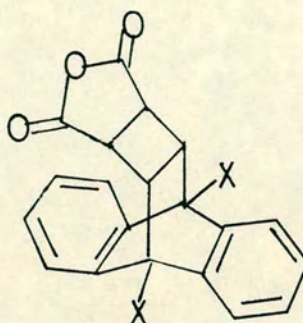
c. Preparation of  54

d. FVP of



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e. Preparation of anhydrides



i) X=H

55

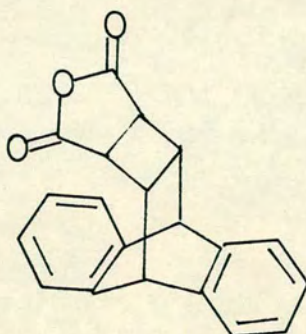
ii) X=Br

56

iii) X=Ph

56

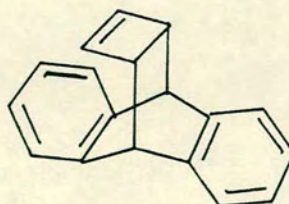
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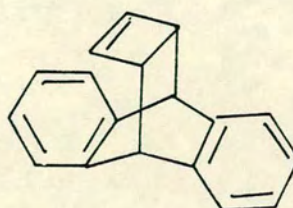
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and its derivatives

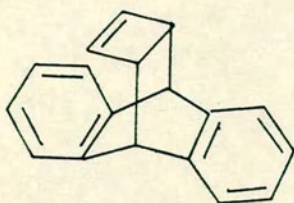


a. Preparation of



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b. FVP of



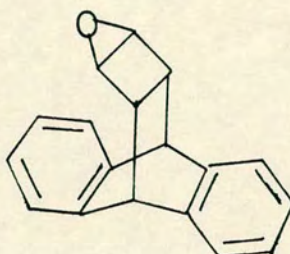
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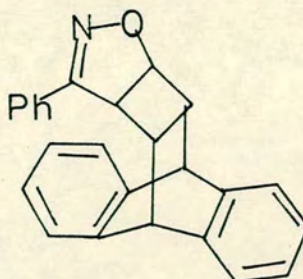
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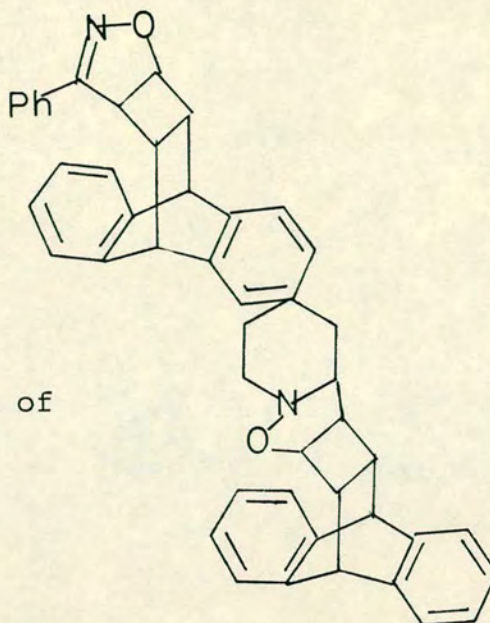
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b. FVP of

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c. Preparation of

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d. FVP of

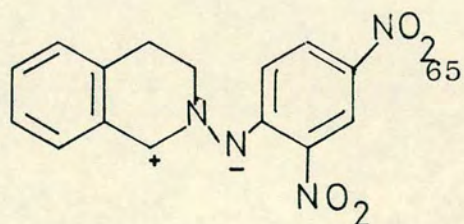
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e. Attempted reaction with EtO_2CN_3

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f. Attempted reaction with



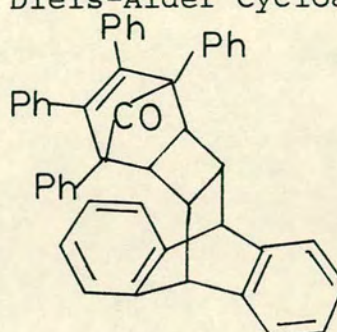
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65

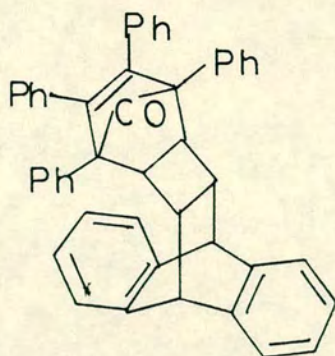
4. Preparation and FVP of Diels-Alder Cycloadducts

a. Preparation of

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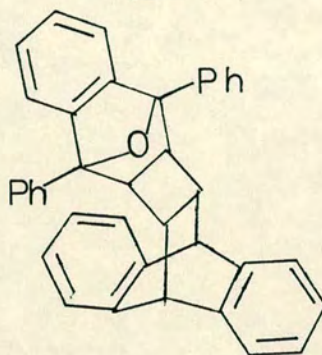


b. FVP of



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c. Preparation of



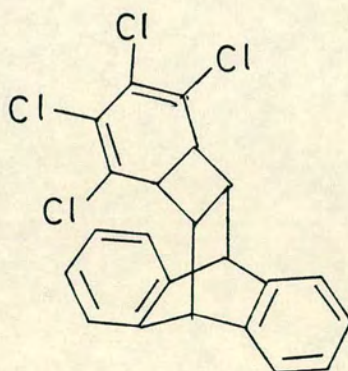
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e. Preparation of



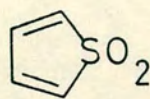
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f. FVP of

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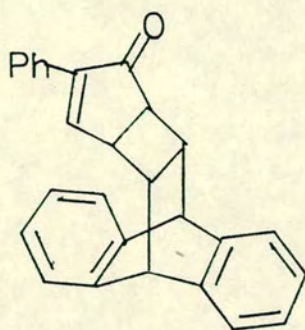
g. Attempted reaction with



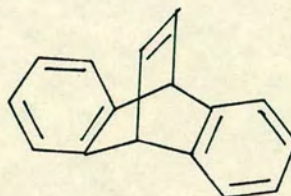
69

h. FVP of

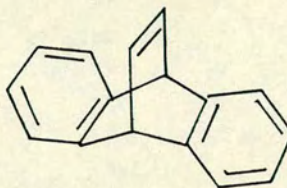
70



E. Preparation and FVP of
and its derivatives



1. Preparation and FVP of



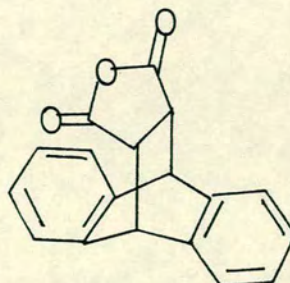
a. Attempted preparation of

"

72

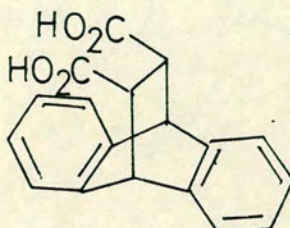
i) Preparation of

72

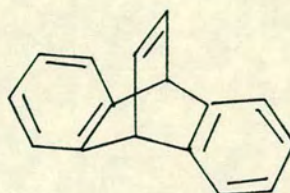


ii) Preparation of

72



- iii) Attempted preparation
of
using $\text{Pb}(\text{OAc})_4$



73

- iv) Preparation of
using $\text{Ni}(\text{PPh}_3)_2(\text{CO})_2$

"

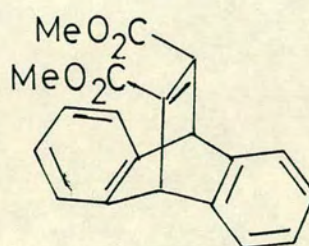
73

- b. Preparation of

"

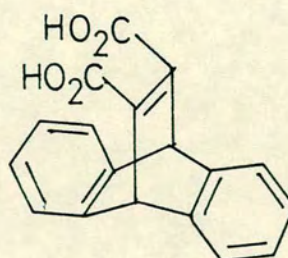
74

- i) Preparation of



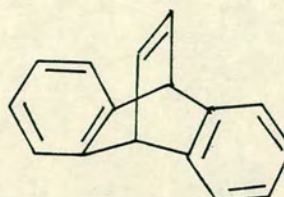
74

- ii) Preparation of



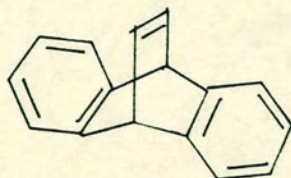
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- iii) Preparation of



75

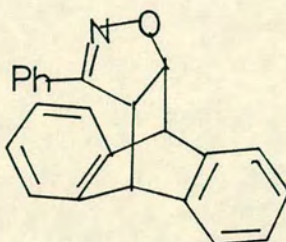
c. FVP of



76

2. Reaction with 1,3 dipoles and FVP of adducts

a. Preparation of



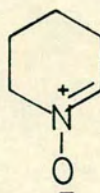
76

b. FVP of

"

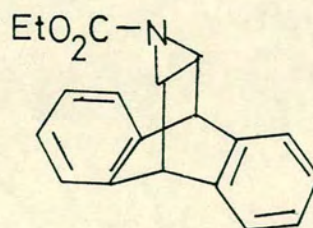
77

c. Attempted reaction with



77

d. Preparation of



78

e. FVP of

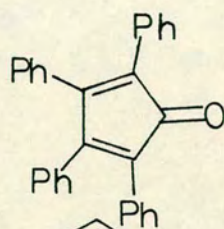
"

78

f. Attempted reaction with $p\text{-MeO-C}_6\text{H}_4\text{C}^{\dagger}\text{=N-S}^-$ 79

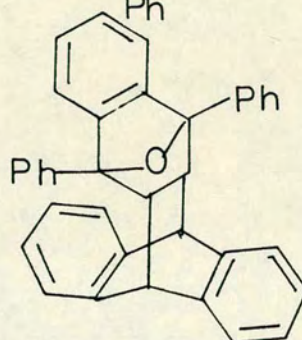
3. Preparation and FVP of Diels-Alder Cycloadducts

a. Attempted reaction with



79

b. Preparation of



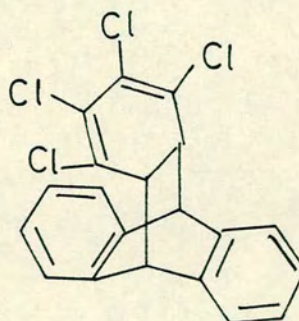
80

c. FVP of

"

80

d. Preparation of



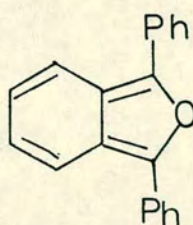
81

e. FVP of

"

82

f. FVP of



82

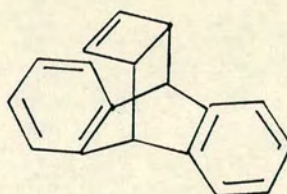
F. Polymerisation Reactions of Cyclic Alkenes via Metathesis

1. Polymerisation of



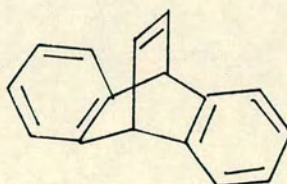
83

2. Polymerisation of



83

3. Attempted metathesis of



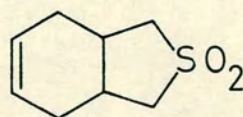
84

4. Attempted metathesis of



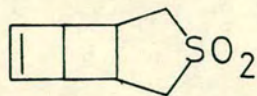
84

5. Attempted metathesis of



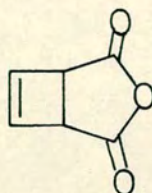
85

6. Attempted metathesis of



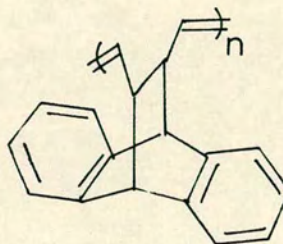
85

7. Attempted metathesis of



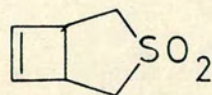
85

8. Extrusion of anthracene from



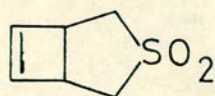
86

G. Preparation and FVP of



and Adducts

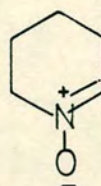
1. Preparation of



87

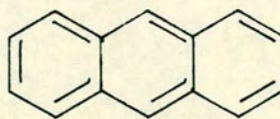
2. Reaction with 1,3 dipoles

a. Attempted reaction with



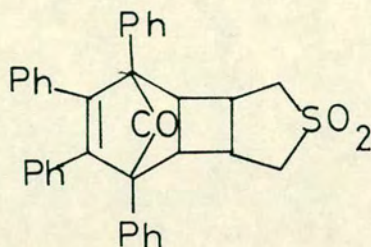
88

b. Attempted reaction with



89

c. Preparation of



89

d. FVP of

"

90

at 330°C

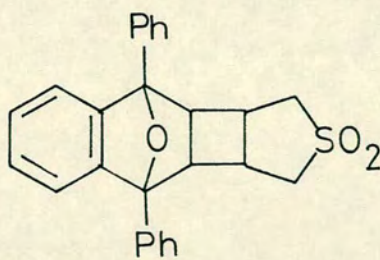
e. FVP of

"

90

at 675°C

f. Preparation of



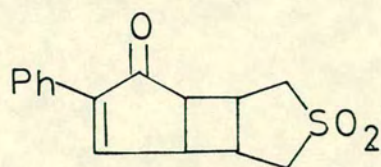
91

g. FVP of

"

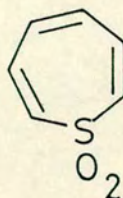
91

h. FVP of

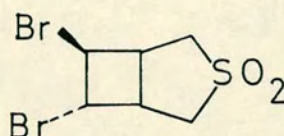


92

4. Attempted preparation of

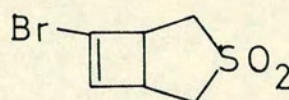


a. Preparation of



93

b. Preparation of



93

c. Reaction of

"

94

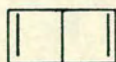
with various bases

d. Photolysis of

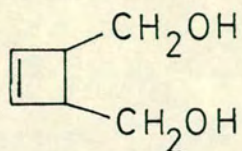
"

94

H. Synthesis of

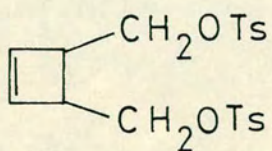


1. Preparation of



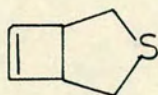
95

2. Preparation of



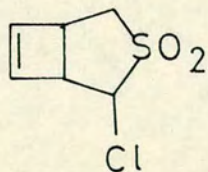
95

3. Preparation of



96

4. Preparation of



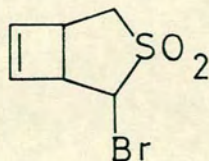
96

5. Reaction of
with KOBU^t

"

97

6. Preparation of



98

A. Symbols and Abbreviations

mmol	millimoles
M	mol dm^{-3}
m.p.	melting point
b.p.	boiling point
h, min,	hours, minutes
g.c.	gas liquid chromatography
g.c.-m.s.	gas liquid chromatography - mass spectroscopy
n.m.r.	nuclear magnetic resonance
δ	chemical shift
s,d,t,q,m	singlet, doublet, triplet, quartet, multiplet
J	spin-spin coupling constant
quat.C	^{13}C n.m.r., quaternary carbon
i.r.	infra red
ν	wavenumber
m.s.	mass spectroscopy
M^+	mass of molecular ion
m/z	mass to charge ratio
FVP	flash vacuum pyrolysis

B. Instrumentation and General Techniques

1. Nuclear Magnetic Resonance Spectroscopy (n.m.r.)

a. ^1H -n.m.r.

Routine spectra were obtained at 60MHz on a Varian EM-360 spectrometer and a Bruker WP80, operated by Mr. L.H. Bell. Spectra of new compounds and decoupling studies were obtained at 100MHz on a Varian 100MHz spectrometer and at 200MHz on a Bruker WP200 spectrometer, both machines were operated by Mr. J.R.A. Millar. High resolution and selectively decoupled spectra were obtained at 360MHz on a Bruker WH-360 spectrometer operated by Dr. I.H. Sadler and Dr. D. Reed.

b. ^{13}C -n.m.r.

Routine spectra were obtained at 25MHz on a Varian CFT-20 spectrometer operated by Mr. J.R.A. Millar. Spectra of small samples were obtained at 90MHz on a Bruker WH-360 spectrometer operated by Dr. I.H. Sadler and Dr. D. Reed and at 50MHz on a Bruker WP200 spectrometer operated by Mr. J.R.A. Millar.

All chemical shifts are expressed in parts per million to high frequency of tetramethylsilane.

2. Infrared Spectroscopy

Spectra were obtained on a Perkin-Elmer 157G grating spectrometer and a Perkin Elmer 781 infrared spectrophotometer. Unless otherwise stated, solids were run as nujol mulls and liquids as thin films, both on sodium chloride plates. Spectra were calibrated with the polystyrene peak at 1603 cm^{-1} .

3. Mass Spectroscopy

Mass spectra and accurate mass measurements were obtained on an A.E.I. ms-902 instrument operated by Mr. D.J.A. Thomas.

4. Gas Chromatography-Mass Spectroscopy

The g.l.c.-m.s. measurements were obtained on a Pye series 104 chromatograph coupled to a V.G. Micromass 12 spectrometer and operated by Miss E. Stevenson.

5. Elemental Analyses

Microanalyses for carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer 240 Elemental Analyser by Mr. J. Grunbaum, University of Edinburgh.

6. Melting Points

Routine melting points were determined using an Electro-thermal melting point apparatus while melting points of new compounds were determined on a Reichert hot-stage microscope. All melting points are uncorrected.

7. Gas Liquid Chromatography

A Pye 104 chromatograph with a flame ionisation detector was used with nitrogen as a carrier gas and a 2m x 4.5mm glass column. The columns used were 10% polyethyleneglycoladipate (PEGA), 5% silicon elastomer (SE30) and 5% carbowax 20M, all on Chromosorb W (80-100 mesh).

8. Preparative Gas Chromatography

Preparative g.l.c. was carried out using a Carlo Erba Strumentazione Fractovap 2450 instrument. The columns used were 0.85m x 12mm columns of 30% PEGA and of 5% carbowax 20M, both on Chromosorb A (40-60 mesh) and the products were collected in traps cooled by dry ice-acetone.

9. Thin Layer Chromatography

This was carried out using 0.3mm layers of alumina (Merck, neutral aluminium oxide 60G, Type E) or silica (Merck, Kieselgel 60G), containing 0.5% Woelm fluorescent green indicator, on glass plates. The components were observed under ultraviolet light or by their reaction with iodine vapour.

10. Preparative Thin Layer Chromatography

This was carried out using 1.0mm layers of the supports mentioned above. After locating the components with iodine or UV light, the bands were scraped off and the products removed from the support by soaking with 5% A.R. methanol in chloroform for 3 h.

11. Column Chromatography

Alumina was of Laporte Industries Alumina H (100-200 mesh), deactivated by addition of 6% water. Silica was of Fisons Scientific Apparatus - Silica Gel for chromatography (60-120 mesh) and was 10% deactivated.

12. Drying and Evaporation of Organic Solutions

Organic solutions were dried over anhydrous magnesium sulphate for several hours and were evaporated under reduced pressure on a rotary evaporator.

13. Photochemical Reactions

The lamps used were 125W and 400W medium pressure water cooled mercury lamps supplied by Applied Photophysics Ltd., London. Large scale reactions were carried out by inserting the quartz or pyrex reactor well in a vessel containing the reaction mixture. Small scale reactions could be performed by attaching a quartz tube containing the reaction mixture to the side of the reactor well.

14. Drying and Purification of Materials used

a. Drying and Purification of Solvents

Commercially available solvents were used without further purification unless otherwise indicated. Where pure methanol, chloroform or toluene were required the commercial Analytical Reagent (A.R.) grade solvent was used. Dry ether was prepared by addition of sodium wire and dry benzene and toluene were prepared by addition of sodium wire to the A.R. grade solvents. Dry dichloromethane and carbon tetrachloride (b.p. 77.5°C) were distilled from phosphorus pentoxide and stored over molecular sieve. Pyridine was dried by heating under reflux with potassium hydroxide for 2 h and then distilling (b.p. $114-117^{\circ}\text{C}$) onto molecular sieve. Dry tetrahydrofuran, dimethoxyethane and dimethylformamide were prepared by heating

the solvent under reflux with calcium hydride in an atmosphere of dry nitrogen for 2 h and then distilling onto molecular sieve. Ethyl acetate was purified and dried by the method of Vogel²⁷ (b.p. 77-79°C) and was stored over molecular sieve. "Pet.-ether" refers to light petroleum, the redistilled 40-60°C boiling fraction being usual as a reaction solvent for chromatography, and the 60-80°C fraction being used for recrystallisation. Solvent ratios are given as volume/volume.

b. Purification and Drying of Reagents and Solvents for Metathesis Reactions

Chlorobenzene was dried by heating under reflux with phosphorus pentoxide in an atmosphere of nitrogen for 2 h and then distilled onto molecular sieve before use. 2-Norbornene (Aldrich) was purified by distillation from potassium. Tungsten hexachloride (Aldrich) was sublimed immediately before use, taking great care to allow no water vapour or air to come in contact with the resublimed material. Tetramethyl tin was stored over molecular sieve.

c. Drying of Gases

In all cases nitrogen was dried by passing the gas through concentrated sulphuric acid followed by calcium chloride before use.

15. Flash Vacuum Pyrolysis

The apparatus used was based on the design of W.D. Crow, Australian National University. A similar set-up is illustrated in the recent monograph by Brown.⁶²

The essential features of the apparatus are shown in Fig. 2 . .A sample was volatilised from a tube, heated in

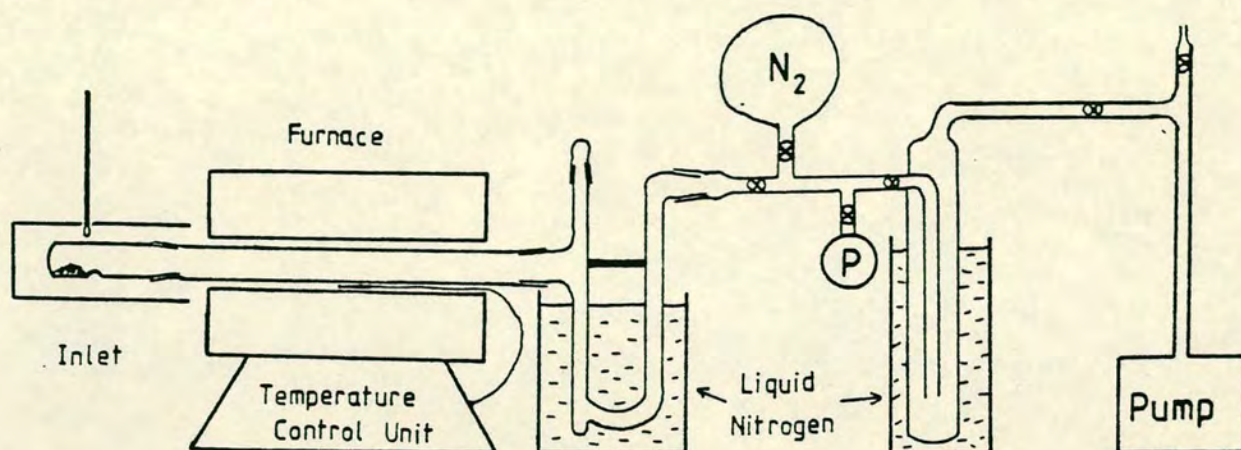


Fig. 2

a Buchi Kugelrohr oven, through a 30 x 2.5 cm silica tube. This was heated at temperatures in the range 350-900°C by a Stanton Redcroft laboratory tube furnace LM8100, the temperature being measured by a Pt/Pt -13% Rh thermocouple situated at the centre of the furnace. The products were collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of 10^{-2} - 10^{-3} mmHg by an Edwards Model ED100 high capacity rotary oil pump, the pressure being measured by a Pirani gauge situated between the trap and the pump. Under these conditions the contact time in the hot zone was estimated to be in the range 1-10 milliseconds. In some cases it was desirable to increase the contact time and this was achieved by packing the furnace tube with 5 cm lengths of silica tubing or a plug of silica wool.

The pyrolysis conditions are quoted as follows: "(weight

of material volatilised, furnace temperature, average pressure during the pyrolysis, inlet temperature)".

Small scale pyrolyses were generally carried out using 25-100 mg of material. After the pyrolysis the system was isolated from the pump and filled with nitrogen gas. The product was then dissolved out of the trap in deuteriochloroform and analysed directly by ^1H -n.m.r. By adding the chloroform while the trap was still frozen and keeping the solution cold, volatile or unstable products could be isolated in high yield. Yields were estimated by adding 5-10 mg of a solvent such as dichloromethane and comparing the n.m.r. integrals. This calibration was estimated to be accurate to $\pm 10\%$.

In large scale pyrolyses 0.2-1.0 g of material was used and after filling the system with nitrogen the product was dissolved out and purified by the normal methods.

C. Preparation and Reactions of 2,4-Dioxo-3-oxabicyclo-[3.2.0]hept-6-ene

1. Preparation of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene

The title compound was prepared according to the method of Bloomfield *et al.*,⁶³ which was an adaptation of Hartmann's⁶⁴ original method.

Maleic anhydride (25 g, 255 mmol) was irradiated in the presence of acetylene by a 400W medium pressure mercury lamp in a solution of ethyl acetate (500 ml) containing benzo-phenone (10 g, 54 mmol) at -78°C for 30 h, $\lambda=300\text{nm.}$ After warming the solution to room temperature the ethyl acetate was evaporated and the residue was distilled to give unreacted maleic anhydride followed by the desired product (16.5 g) b.p. $120-135^{\circ}\text{C}/2\text{ mmHg}$. Recrystallisation from diisopropyl ether gave 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (15.8 g, 49%) as colourless needles, m.p. $86-87^{\circ}\text{C}$ (lit.,⁶³ 89°C).

2. Reaction with 1,3-dipoles

a. Attempted photochemical reaction with ethyl azidoformate

A mixture of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (119 mg, 0.96 mmol) and ethyl azidoformate (0.508 g, 4.4 mmol) in a quartz n.m.r. tube was irradiated at 400W for a total of 48 h. (After 28 h the evolution of nitrogen from the reaction had ceased). The ^1H n.m.r. of the reaction was observed periodically and showed no decrease in intensity of the double bond of the starting material.

b. Reaction with *p*-methoxybenzonitrile oxide

Triethylamine (0.440 g, 4.36 mmol) was added to a stirred solution of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (0.541 g, 4.36 mmol) and *p*-methoxybenzohydroximoyl chloride (0.810 g, 4.36 mmol) in tetrahydrofuran (40 ml). The reaction mixture was allowed to stir at room temperature for 3 h. After this time period the white precipitate of triethylamine hydrochloride (0.560 g, 93% activation of the 1,3-dipole) which had formed was filtered off. The filtrate was evaporated to dryness to give a yellow gum (1.19 g), which did not give a solid on trituration with ether. The ^1H -n.m.r. spectrum showed that an acidic proton peak δ_{H} 9.7 was present therefore hydrolysis had occurred to give the diacid.

c. Preparation of dimethyl 4-(*p*-methoxyphenyl)-2-oxa-3-azabicyclo[3.2.0]hept-3-ene-6,7-dicarboxylate

4-(*p*-Methoxyphenyl)-2-oxa-3-azabicyclo[3.2.0]hept-3-ene-6,7-dicarboxylic acid (1.19 g, 4.09 mmol), as a yellow gum, was dissolved in methanol (40 ml), then concentrated sulphuric acid (1 ml) was added and the mixture was heated under reflux for 3 h. The solution was allowed to cool and water (20 ml) was added. The methanol was removed by evaporation and the product was extracted from the aqueous solution with dichloromethane (4 x 25 ml). The dichloromethane extract was dried and evaporated to give a white solid which was recrystallised from ethanol to give dimethyl-4-(*p*-methoxyphenyl)-2-oxa-3-azabicyclo[3.2.0]hept-3-ene-6,7-dicarboxylate (386 mg, 30%) as colourless needles, m.p. 121.5-123°C (Found: C, 60.15; H, 5.35; N, 4.4. $\text{C}_{16}\text{H}_{17}\text{NO}_6$ requires C, 60.3; H, 5.45; N, 4.25%); ν_{max} 1730

(CO), 1610 (C=C), 1520 (-C=N-), 1260 ($\overset{\text{O}}{\parallel}\text{-C-O-C}$) and 1180 cm^{-1} ($\overset{\text{O}}{\parallel}\text{-C-O-C}$); δ_{H} (100MHz; solvent CDCl_3) 3.63 (2H, dd, C(6)H and C(7)H), 3.70 (3H, s, $-\text{OCH}_3$), 3.76 (3H, s, $-\text{OCH}_3$), 3.82 (3H, s, $-\text{OCH}_3$), 4.42 (1H, dd, J 8 and 3Hz, C(5)H), 5.56 (1H, dd, J 8 and 3Hz, C(1)H), 6.89 (2H, d, J 7Hz, Ar) and 7.59 (2H, d, J 7Hz, Ar); m/z 319 (M^+ , 38%), 260 (11), 228 (16), 205 (9.5), 200 (8), 175 (100), 160 (8), 147 (19), 133 (16) and 113 (46).

d. Attempted reaction with *p*-nitrobenzohydroximoyl chloride

Triethylamine (0.814 g, 8.06 mmol) was added to a stirred solution of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (0.997 g, 8.04 mmol) and *p*-nitrobenzohydroximoyl chloride (1.62 g, 8.05 mmol) in tetrahydrofuran (40 ml). The mixture was stirred at room temperature for 3 h. The triethylamine hydrochloride (0.68 g, 62% activation of the dipole) was then filtered off and the tetrahydrofuran was evaporated from the filtrate to afford a brown gum (2.09 g). The ^1H -n.m.r. spectrum of the gum showed that the anhydride group had partially hydrolysed to the diacid and that the double bond of the anhydride was still present.

The gum (2.09 g) was dissolved in methanol (40 ml) and concentrated sulphuric acid (1 ml) was added. The mixture was heated under reflux for 6 h. After the reaction mixture was allowed to cool, water (20 ml) was added and the methanol was evaporated. The organic product was extracted from the aqueous solution with dichloromethane (4 x 25 ml). The extract was dried and evaporated to dryness to give a brown

gum (1.24 g). Chromatography on silica gel with ether-hexane (1:1) as eluant yielded three fractions, none of which were identifiable by ^1H -n.m.r. as the desired product.

Further attempts to react the *p*-nitrobenzonitrile oxide with 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene met with failure. The attempts included heating the two reactants together in boiling toluene and the addition of the *p*-nitrobenzohydroximoyl chloride in ether to an ethereal solution of the alkene and triethylamine, which was the method reported by Rieber and Bohm.⁶⁵

e. Attempted reaction with ethyl oxalimoyl chloride

A solution of ethyl oxalimoyl chloride (1.106 g, 7.3 mmol) and 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (0.913 g, 7.3 mmol) in tetrahydrofuran (40 ml) was treated with triethylamine (0.737 g, 7.3 mmol) and was allowed to stir for 18 h at 20°C. The triethylamine hydrochloride (0.752 g, 75% activation of dipole) was filtered off and the tetrahydrofuran was evaporated. The i.r. spectrum of the remaining yellow oil showed that both the anhydride and diacid functional groups were present.

The gum (2.07 g) was dissolved in methanol (40 ml) and concentrated sulphuric acid (1 ml) was added. The mixture was heated under reflux for 8 h and then water (20 ml) was added. The methanol was evaporated and the aqueous solution was extracted with dichloromethane (3 x 50 ml). The extract was dried and evaporated to dryness to afford a yellow oil which was examined by ^1H -n.m.r. which showed dimethyl cyclobut-3-ene 1,2-dicarboxylate as the main product.

An attempt was made to increase the reactivity of the

dipole by heating the starting materials in a solution of toluene for 64 h. $^1\text{H-N.m.r.}$ spectroscopy showed that the olefinic protons, $\delta 6.4$, of the alkene were still present and indicated that no reaction had occurred.

f. Attempted reaction with *p*-anisonitrile sulphide

A solution of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (0.296 g, 2.39 mmol) and 5-(*p*-methoxyphenyl)-[1,3,4]-oxathiazol-2-one (0.500 g, 2.39 mmol) in dry xylene (10 ml) was heated under reflux for 120 h. The xylene was evaporated to give a brown gum which was redissolved in ethanol and the resulting precipitate of sulphur was removed. The ethanol was evaporated to afford a brown oil (0.652 g) which gave a $^1\text{H-n.m.r.}$ spectrum which showed that the starting anhydride was present. The i.r. spectrum showed a peak at ν_{max} 2220 cm^{-1} which indicated that the nitrile sulphide had been generated and had decomposed to give the nitrile rather than react with the alkene.

g, Attempted reaction with an azomethine imine

(i) 1-Ethoxy-2-(2,4-dinitroanilino)-1,2,3,4-tetrahydroisoquinoline

This was prepared in four steps (38% overall yield by the method of Schmitz^{66,67} as orange flakes, m.p. $136-138^\circ\text{C}$ (lit.⁶⁶ $137-140^\circ\text{C}$).

(ii) Attempted reaction with the azomethine imine

A solution of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (0.16 g, 1.3 mmol) and 1-ethoxy-2-(2,4-dinitroanilino)-1,2,3,4-tetrahydroisoquinoline (0.46 g, 1.3 mmol) in A.R. toluene (55 ml) was heated under reflux for 24 h. The toluene was



evaporated to give yellow brown crystals (0.50 g) whose ^1H -n.m.r. showed only the dipole dimer (hexahydrotetrazine⁶⁸), and the starting material to be present.

h. Attempted reaction with diphenylnitrile imine

A solution of diphenylhydrazidoyl chloride (0.310 g, 1.34 mmol) in dry ether (20 ml) was added dropwise to a stirred solution of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (0.166 g, 1.34 mmol) and triethylamine (0.148 g, 1.46 mmol) in dry ether (30 ml) and allowed to stir at 20°C for 120 h. The precipitate of triethylamine hydrochloride (0.155 g, 77% activation of dipole) which had formed was filtered off. The ether was evaporated from the filtrate to give a yellow waxy solid whose ^1H -n.m.r. spectrum showed that the starting anhydride and the 1,3,4,6-tetraphenyl-1,4-dihydro-s-tetrazine,⁶⁹ formed by dimerisation of the nitrile imine, were present.

3. FVP of 1,3-Dipole Adducts

a. FVP of 6,7-dimethoxycarbonyl-4-(p-methoxyphenyl)-2-oxa-3-azabicyclo[3.2.0]hept-3-ene

FVP of the title compound (104 mg, 600°C, 7×10^{-3} mmHg, inlet 90-120°C) gave a yellow oil whose ^1H n.m.r. spectrum showed the presence of an isoxazole ring δ 6.58 (1H, d, J 3Hz) and 8.40 (1H, d, J 3Hz). Preparative t.l.c. on silica gel with ether/*n*-hexane (3:1) as eluant gave 3-(p-methoxyphenyl) isoxazole (49 mg, 64%); δ_{H} (100MHz; CDCl_3) 3.82 (3H, s, -OCH₃), 6.58 (1H, d, J 3Hz, C(4)H), 6.95 (2H, d, J 9Hz, Ar), 7.77 (2H, d, J 9Hz, Ar) and 8.38 (1H, d, J 3Hz, C(5)H) which was identical to the literature spectrum.⁷⁰

4. Reaction with 1,3-Dienes

a. Preparation of 1,9,10,11-tetraphenyl-4,6,12-trioxo-5-oxatetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodec-10-ene

A solution of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (0.25 g, 2.0 mmol) and tetraphenylcyclopentadienone (0.77 g, 2.0 mmol) in anhydrous benzene (50 ml) was heated under reflux for 18 h. The benzene was evaporated to give a dark purple residue which was triturated with ice-cold ether to afford a pale purple crystalline solid. Recrystallisation from chloroform (twice) gave 1,9,10,11-tetraphenyl-4,6,12-trioxo-5-oxatetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodec-10-ene (0.43 g, 42%) as colourless crystals, m.p. 234-235°C (with decomposition) (Found: C, 82.9; H, 4.85. C₃₅H₂₄O₄ requires C, 82.7; H, 4.75%); ν_{\max} 1865 (C=O), 1790 (C=O), 1780 (C=O), 1600 (aromatic ring) and 1030 cm⁻¹ (anhydride C-O-C); δ_{H} (100MHz; (CD₃)₂CO) 3.30-3.22 (2H, m, C(2)H and C(8)H), 4.00-3.92 (2H, m, C(3)H and C(7)H), 6.90 (10H, s, Ph) and 7.40-7.14 (10H, m, Ph); m/z 508 (M⁺, 2.6%), 480 (15), 452 (26), 383 (53) and 382 (100).

b. FVP of 1,9,10,11-tetraphenyl-4,6,12-trioxo-5-oxatetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodec-10-ene

FVP of the title compound (52 mg, 525°C, 6 x 10⁻³ mmHg, inlet 180-195°C) gave a white solid at the liquid nitrogen level of the trap and a yellow liquid at the exit of the furnace. The white solid was shown by its ¹H-n.m.r. spectrum to be maleic anhydride. Preparative t.l.c. of the yellow liquid on silica with ether-*n*-hexane (1:10) as eluant gave 1,2,3,4-tetraphenylbenzene (17 mg, 45%) as a white solid which was identified by

its ^1H -n.m.r. spectrum.⁷¹ Confirmation was given by t.l.c. of the sample on silica with Pet-Ether (40-60) as eluant against an authentic sample.

FVP at 350°C gave the same result but with a lower yield (12%)

c. Preparation of 1,9-diphenyl-4,6-dioxo-5,12-dioxa-10,11-benzotetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodec-10-ene

A solution of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (0.469 g, 3.8 mmol) and 1,3-diphenylisobenzofuran (1.072 g, 3.9 mmol) in dry benzene (80 ml) was heated under reflux for 4 h. During this time the yellow fluorescence of the solution had reduced considerably in intensity and t.l.c. confirmed that most of the 1,3-diphenylisobenzofuran had reacted. The benzene was evaporated to afford white crystals and recrystallisation from chloroform/*n*-hexane (2:1) gave 1,9-diphenyl-4,6-dioxo-5,12-dioxa-10,11-benzotetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodec-10-ene (1.021 g, 68%) as colourless needles. The product was sublimed (150°C at 0.3 mmHg) to give analytically pure colourless prisms m.p. $268-269^\circ\text{C}$ (Found: C, 78.9; H, 4.45. $\text{C}_{26}\text{H}_{18}\text{O}_4$ requires C, 79.2; H, 4.6%); ν_{max} 1865 (anhydride C=O), 1855 (C=O), 1790 (C=O), 1196, 1075, and 910 cm^{-1} ($\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$); δ_{H} (100MHz; CDCl_3) 3.11 (2H, dd, J 2 and 1Hz, C(2)H and C(8)H), 3.30 (2H, dd, J 2 and 1Hz, C(3)H and C(7)H), 6.80-7.04 (2H, m, Ar), 7.04-7.26 (2H, m, Ar) and 7.40-7.74 (10H, m, Ph); m/z 394 (M^+ , 55%), 296 (8), 270 (100), 241 (9), 165 (8), 135 (7), 105 (9) and 77 (13).

d. FVP of 1,9-diphenyl-4,6-dioxo-5,12-dioxa-10,11-benzotetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodec-10-ene

FVP of the title compound (27 mg, 600°C , 6×10^{-3} mmHg,

inlet 200-205°C) gave a fluorescent yellow solid (19 mg) at the exit of the furnace and a white solid (5 mg) at the liquid nitrogen level of the trap. The white solid was shown by its ^1H n.m.r. spectrum to be maleic anhydride. The yellow solid was shown by its ^1H n.m.r. spectrum to be 1,3-diphenylisobenzofuran, this was confirmed by comparison with an authentic by t.l.c. The ^1H -n.m.r. spectrum also showed that a small amount of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene was present in the 1,3-diphenylisobenzofuran component.

e. Preparation of anhydrides

(i) Preparation of 4,6-dioxo-5-oxa-10,11:12,13-dibenzotetracyclo[7.2.2.0^{2,8}.0^{3,7}]trideca-10,12-diene

A mixture of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (6.0 g, 48 mmol) and anthracene (8.6 g, 48 mmol) in dry toluene (300 ml) was heated under reflux for 168 h. The solvent was evaporated to give a white solid which was purified by sublimation (150°C, 0.2 mmHg) to give 4,6-dioxo-5-oxa-10,11:12,13-dibenzotetracyclo[7.2.2.0^{2,8}.0^{3,7}]trideca-10,12-diene (11.4 g, 78%) as colourless crystals m.p. 255-256°C (Found: C, 79.2; H, 4.55. $\text{C}_{20}\text{H}_{14}\text{O}_3$ requires C, 79.45; H, 4.65%); ν_{max} 1860 (C=O), 1780 (C=O), 1230, 1060 and 910 cm^{-1} ($\begin{smallmatrix} \text{O} & & \text{O} \\ \parallel & & \parallel \\ \text{C}-\text{O}-\text{C} \end{smallmatrix}$); δ_{H} (100MHz; CDCl_3) 2.52-2.60 (2H, m, C(2)H and C(8)H), 2.88 (2H, m, C(3)H and C(7)H), 4.50 (2H, t, J 2Hz, C(1)H and C(9)H) and 7.04-7.42 (8H, m, Ar) m/z 302 (M^+ , 58%), 229 (16), 202 (13), 178 (100), 152 (16) and 101 (26).

(ii) Preparation of 1,9-dibromo-4,6-dioxo-5-oxa-10,11:12,13-dibenzotetracyclo[7.2.2.0^{2,8}_{0^{3,7}}]^{3,7}trideca-10,12-diene

A mixture of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (2.0 g, 16.1 mmol) in 9,10-dibromoanthracene (5.6 g, 16.7 mmol) in dry toluene (140 ml) was heated under reflux for 168 h. The solvent was evaporated to give a white solid whose ¹H-n.m.r. spectrum showed that very little of the starting materials remained. Recrystallisation from diisopropyl ether gave 1,9-dibromo-4,6-dioxo-5-oxa-10,11:12,13-dibenzotetracyclo[7.2.2.0^{2,8}_{0^{3,7}}]^{3,7}trideca-10,12-diene (6.6 g, 86%) as white crystals m.p. 185-186°C (Found: C, 52.4; H, 2.55. C₂₀H₁₂Br₂O₃ requires C, 52.15; H, 2.65); ν_{\max} 1860 (C=O), 1780 (C=O) 1230, 1070 and 975 cm⁻¹ ($\begin{smallmatrix} O & O \\ || & || \\ -C & -C- \end{smallmatrix}$); δ_H (100MHz; CDCl₃) 2.58-2.70 (2H, m, C(2)H and C(8)H), 3.18-3.32 (2H, m, C(3)H and C(7)H), 7.18-7.44 (4H, m, Ar) and 7.68-7.84 (4H, m, Ar); m/z 460 (M⁺, 25%), 336 (100), 228 (27), 202 (16), 200 (13), 176 (14), 124 (23), 122 (30), 104 (15) and 102 (13).

(iii) Preparation of 1,9-diphenyl-4,6-dioxo-5-oxa-10,11:12,13-dibenzotetracyclo[7.2.2.0^{2,8}_{0^{3,7}}]^{3,7}trideca-10,12-diene

A mixture of 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (0.37 g, 3.0 mmol) and 9,10-diphenylanthracene (1.00 g, 3.0 mmol) in dry toluene (120 ml) was heated under reflux for 69 h. The solvent was evaporated to give a yellow-white solid whose ¹H-n.m.r. spectrum showed that none of the starting materials remained. Recrystallisation from diisopropyl ether gave 1,9-diphenyl-4,6-dioxo-5-oxa-10,11:12,13-dibenzotetracyclo[7.2.2.0^{2,8}_{0^{3,7}}]^{3,7}trideca-10,12-diene (0.74 g, 53%) as off-white

crystals m.p. $>300^{\circ}\text{C}$ (Found: C, 84.75; H, 5.1.

$\text{C}_{32}\text{H}_{22}\text{O}_3$ requires C, 84.6; H, 4.9%); ν_{max} $\overset{\text{O}}{\underset{\text{O}}{\text{1860}}}$ (C=O), 1785 (C=O), $\overset{\text{O}}{\underset{\text{O}}{\text{1600}}}$ (C=C), 1230, 1065 and $\overset{\text{O}}{\underset{\text{O}}{\text{930}}}$ cm^{-1} (C-O-C); δ_{H} (100MHz; CDCl_3) 1.68-1.80 (2H, m, C(2)H and C(8)H), 2.42-2.56 (2H, m, C(3)H and C(7)H), 6.76-7.00 (8H, m, Ar) and 7.06-7.90 (10H, broad m, Ph); m/z 454 (M^+ , 4%), 330 (100) and 1252 (29).

f. FVP of 4,6-dioxo-5-oxa-10,11:12,13-dibenzotetracyclo-[7.2.2.0^{2,8}.0^{3,7}]trideca-10,12-diene

FVP of the title compound (52 mg, 600°C , 6×10^{-3} mmHg, inlet 200°C) gave a white solid (43 mg) at the exit of the furnace. The ^1H -n.m.r. spectrum of the product showed that a retro-Diels-Alder reaction had taken place to give anthracene and 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene. The ^1H -n.m.r. spectrum showed the yields to be anthracene (65%) and 2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene (35%).

D. Preparation and FVP of 7,8:9,10-dibenzotricyclo-
[4.2.2.0^{2,5}]deca-3,7,9-triene and its adducts

1. Preparation and FVP of 7,8:9,10-dibenzotricyclo-
[4.2.2.0^{2,5}]deca-3,7,9-triene

a. Preparation of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]-
deca-3,7,9-triene

(i) 7,8:9,10-Dibenzotricyclo[4.2.2.0^{2,5}]deca-7,9-diene-
3,4-dicarboxylic acid

4,6-Dioxo-5-oxa-10,11:12,13-dibenzotetracyclo[7.2.2.0^{2,8}-0^{3,7}]trideca-10,12-diene (prepared in Section C.3.f(i)) (18.56 g, 61.5 mmol) was dissolved in a boiling aqueous solution of sodium hydroxide (0.63M, 250 ml). The solution was allowed to cool and then acidified to pH5 with hydrochloric acid (4M). This caused precipitation of a white solid which was filtered off and washed with water. Recrystallisation from acetone-water (3:1) gave 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-7,9-diene-3,4-dicarboxylic acid (11.38 g, 58%) as colourless crystals, m.p. 220-223°C (Found: C, 75.2; H, 5.05. C₂₀H₁₆O₄ requires C, 74.95; H, 5.05%); ν_{\max} 2600 (carboxyl OH) and 1710 cm⁻¹ (C=O), δ_{H} (100MHz; (CD₃)₂SO) 2.04-2.14 (2H, m, C(2)H and C(5)H), 2.62-2.78 (2H, m, C(3)H and C(4)H), 4.39 (2H, t, J 1Hz, C(1)H and C(6)H), 6.82-7.39 (8H, m, Ar) and 11.94-12.36 (2H, br s, OH); m/z 320 (M⁺, 6%), 302 (5), 229 (5), 202 (5) and 178 (100).

(ii) 7,8:9,10-Dibenzo[4.2.2.0^{2,5}]deca-3,7,9-triene

A solution of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-

7,9-diene-3,4-dicarboxylic acid (7.5 g, 23.4 mmol), suspended, in dry pyridine (100 ml) was oxygenated by bubbling oxygen through the solution for 20 min. Lead tetraacetate (vacuum dried, 16.4 g, 37.0 mmol) was added in one portion and the reaction mixture was heated to 80°C. After heating for 20 min the evolution of carbon dioxide was complete, the clear dark brown solution was poured into 5% nitric acid (2000 ml) and extracted with dichloromethane (4 x 250 ml). The extract was washed with aqueous sodium hydrogen carbonate, water and then dried. The solvent was evaporated to give a yellow brown solid. The solid was extracted with boiling ether to give a yellow ethereal solution and a dark brown insoluble solid which was filtered off. The ether was evaporated from the filtrate and the resulting yellow solid was dissolved in ethanol and heated under reflux with activated charcoal for 5 min. The charcoal was filtered off and the solution cooled to give 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (1.87 g, 32%) as colourless crystals, m.p. 141-142°C (lit.,⁷² 137°C); δ_{H} (100MHz; CDCl₃) 2.88-3.00 (2H, m, C(2)H and C(5)H), 4.16-4.30 (2H, m, C(1)H and C(6)H), 5.85 (2H, s, C(3)H and C(4)H) and 7.00-7.36 (8H, m, Ar) was identical to the spectrum reported by Murata.⁷³

Chromatography on silica gel with ether as eluant instead of extraction with ether resulted in a lower yield (20%).

b. FVP of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene

FVP of the title compound (46 mg, 700°C, 6×10^{-3} mmHg, inlet 92-120°C) yielded a yellow solid at the exit of the furnace. Recrystallisation of the product from ethanol gave

7,8:9,10-dibenzobicyclo[4.2.2]deca-2,4,7,9-tetraene (37 mg, 80%) as colourless crystals. The ^1H -n.m.r. spectrum δ_{H} (100MHz; CDCl_3) 4.47 (2H, d, J 9Hz, C(1)H and C(6)H), 5.44 (2H, dd, J 4 and 9Hz, C(3)H and C(4)H), 6.22-6.50 (2H, dt, J 3 and 9Hz, C(2)H and C(5)H) and 7.00-7.34 (8H, m, Ar) was identical to the literature ^1H -n.m.r. spectrum⁷⁴ of the authentic sample made by Nenitzescu.

c. Thermolysis of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene

The title compound (40 mg) was dissolved in d^8 toluene, sealed in a n.m.r. tube and heated at 200°C for 21 h. ^1H -n.m.r. studies on the solution showed that no rearrangement had occurred during this time.

2. Preparation and FVP of 4-oxa-8,9:10,11-dibenzotetracyclo[5.2.2.0^{2,6}0^{3,5}]undeca-8,10-diene

a. Preparation of 4-oxa-8,9:10,11-dibenzotetracyclo[5.2.2.0^{2,6}0^{3,5}]undeca-8,10-diene

m-Chloroperoxybenzoic acid (85%, 205 mg, 1.01 mmol) was added in one portion to a stirred solution of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (156 mg, 0.68 mmol) in ethyl acetate (40 ml) and the mixture was heated under reflux for 20 h. The cooled solution was washed with aqueous sodium carbonate, dried and evaporated to dryness to yield a white solid. Recrystallisation of the solid from ethanol gave 4-oxa-8,9:10,11-dibenzotetracyclo[5.2.2.0^{2,6}0^{3,5}]undeca-8,10-diene (141 mg, 85%) as colourless needles, m.p.

228-232°C (Found: C, 87.6; H, 5.55. $C_{18}H_{14}O$ requires C, 87.75; H, 5.75%); δ_H (100MHz; $CDCl_3$) 2.44-2.62 (2H, m, C(2)H and C(6)H), 3.24-3.36 (2H, m, C(3)H and C(5)H), 4.26-4.40 (2H, m, C(1)H and C(7)H), 7.00-7.40 (8H, m, Ar); m/z 246 (M^+ , 2%), 215 (7), 202 (3) and 178 (100).

b. FVP of 4-oxa-8,9:10,11-dibenzotetracyclo[5.2.2.0^{2,6}.0^{3,5}]-undeca-8,10-diene

FVP of the title compound (35 mg, 650°C, 7×10^{-3} mmHg, inlet 126°C) gave a white solid at the exit of the furnace and a solid at the liquid nitrogen level of the trap. The trap was warmed to 20°C and the solid melted, the 1H -n.m.r. spectrum of this material indicated that it was furan (8 mg). Comparison of the sample with furan by g.l.c. on a 5% SE column at 70°C confirmed that the product was furan. The white solid (23 mg, 91%) was shown by its 1H -n.m.r. spectrum to be anthracene.

c. Thermolysis of 4-oxa-8,9:10,11-dibenzotetracyclo[5.2.2.0^{2,6}.0^{3,5}]-undeca-8,10-diene

The title compound (30 mg) was dissolved in $CDCl_3$ and sealed in a n.m.r. tube. The tube was heated at 165°C for 7 days. Periodic observation of its 1H -n.m.r. spectrum showed that no retro-reaction or rearrangement had occurred and that only starting material was present.

3. Reaction with 1,3-dipoles

a. Preparation of 6-phenyl-4-oxa-5-aza-10,11:12,13-dibenzotetracyclo[7.2.2.0^{2,8}.0^{3,7}]-trideca-5,10,12-triene

Benzohydroximoyl chloride (108 mg, 0.65 mmol) was added to a stirred solution of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]-deca-3,7,9-triene (150 mg, 0.65 mmol) in toluene (15 ml) and the solution was heated under reflux for 38 h. T.l.c. on alumina, with ether as eluant, showed that none of the starting alkene remained. The toluene was evaporated to give an off-white solid which was recrystallised from ethanol-chloroform (9:1) to afford 6-phenyl-4-oxa-5-aza-10,11:12,13-dibenzotetracyclo[7.2.2.0^{2,8}0^{3,7}]trideca-5,10,12-triene (180 mg, 79%) as colourless needles, m.p. 226-228°C (Found: C, 85.8; H, 5.25; N, 3.9. C₂₅H₁₉NO requires C, 85.9; H, 5.5; N, 4.0%); ν_{\max} 1560 cm⁻¹ (C=N); δ_{H} (100MHz; CDCl₃) 2.56-2.96 (2H, m, C(2)H and C(8)H), 3.32 (1H, dd, J 7 and 2Hz, C(7)H), 4.21 (1H, dd, J 7 and 2Hz, C(3)H), 4.49 (2H, d, J 3Hz, C(1)H and C(9)H) and 6.92-7.83 (13H, m, Ar); m/z 349 (M⁺, 17%), 205 (100), 203 (100) and 178 (100).

b. FVP of 6-phenyl-4-oxa-5-aza-10,11:12,13-dibenzotetracyclo[7.2.2.0^{2,8}0^{3,7}]trideca-5,10,12-triene

FVP of the title compound (82 mg, 625°C, 5 x 10⁻³ mmHg, inlet 180°C) gave a yellow solid and a liquid (64 mg) at the exit of the furnace which became purple on contact with air. The ¹H-n.m.r. spectrum of the product showed the presence of anthracene as one of the products. T.l.c. on silica gel with ether as eluant showed 2 main components, g.l.c. on 5% SE30 at 170°C also showed the presence of six components and confirmed the presence of anthracene by comparison with an authentic sample. G.l.c.-m.s. (5% SE30, 170°C) results suggested that 5,6:7,8-dibenzo[2.2.2]octa-2,5,7-triene was present, due to a

parent peak m/z 204, and the presence of this compound was confirmed by comparison on the g.l.c. with an authentic sample. A third compound was found to be 3-phenylisoxazole by comparison on the g.c. of the authentic sample obtained from the reaction in section E.3.b. The g.l.c.-m.s. also indicated that this compound was present by the presence of a compound with a parent peak m/z 145. No other compounds present were positively identified.

c. (i) Preparation of 1-piperidine-1-oxide

This was prepared by the method of Kakisawa.⁷⁵

N-Hydroxypiperidine was treated with yellow mercuric oxide to afford 1-piperidine-1-oxide as a pale yellow oil. The ^1H n.m.r. spectrum was identical to that of the literature value δ_{H} (60MHz; CDCl_3) 1.4-2.2 (4H, m), 3.5-3.9 (2H, m), 3.5-4.0 (2H, m) and 7.2 (1H, m).

(ii) Preparation of 4-oxa-5-amino-14,15:16,17-dibenzopentacyclo[11.2.2.0^{2,12}.0^{3,11}.0^{5,10}]heptdeca-14,16-diene

1-Piperidine-1-oxide (149 mg, 1.51 mmol) was added to a stirred solution of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (346 mg, 1.50 mmol) in toluene (13 ml) and the mixture was heated under reflux for 13 h. T.l.c. on alumina and elution with ether showed reaction of the starting alkene under these conditions. The toluene was evaporated to yield an oily, semi-crystalline material which decomposed on a chromatography column of either alumina or silica to give the starting alkene and other unidentified products. The crude product was therefore purified by three successive recrystallisa-

tions from ethanol to give 4-oxa-5-aza-14,15:16,17-dibenzopentacyclo[11.2.2.0^{2,12}0^{3,11}0^{5,10}]heptdeca-14,16-diene (356 mg, 72%) as pale yellow crystals m.p. 178-181°C (Found: C, 83.75; H, 6.9; N, 4.45. $C_{23}H_{23}NO$ requires C, 83.9; H, 7.05; N, 4.26%; δ_H (100MHz; $CDCl_3$) 0.95-1.45 (4H, m), 1.45-1.73 (2H, m), 1.77-1.95 (1H, m), 2.13-2.32 (1H, m), 2.47-2.62 (1H, m), 2.85-3.12 (2H, m), 3.30-3.48 (1H, m), 3.55-3.73 (1H, m), 4.32 (2H, t, J 3Hz, C(1)H and C(13)H) and 6.98-7.37 (8H, m, Ar); m/z 329 (M^+ , 100%), 178 (85) and 125 (42).

d. FVP of 4-oxa-5-aza-14,15:16,17-dibenzopentacyclo[11.2.2.0^{2,12}0^{3,11}0^{5,10}]heptdeca-14,16-diene

FVP of the title compound (53 mg, 600°C, 7×10^{-3} mmHg, inlet 140-150°C) gave a white solid (20 mg) at the exit of the furnace and a red liquid (13 mg) at the liquid nitrogen level of the trap. The 1H -n.m.r. spectrum of the white solid showed it to be anthracene. On warming the trap to 20°C and on contact with air the red liquid became brown. The 1H n.m.r. spectrum of the liquid showed that anthracene and dibenzobarrelene were present in small quantities. Preparative t.l.c. on silica gel with Petroleum ether (40-60)-ether (2:3) as eluant gave two main components, R_f 0.95 and R_f 0.5, and several minor components. The component at R_f 0.95 (4 mg) was shown by its 1H -n.m.r. spectrum to be anthracene. The component of R_f 0.5 (7 mg) has a 1H -n.m.r. spectrum which showed only aromatic protons, which were not present in the 1H n.m.r. spectrum of crude material. This observation suggested that the product had decomposed during chromatography. The parent peak on the mass spectrum, m/z 362, was unidentifiable.

e. Attempted reaction with ethyl azidoformate

A solution 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (92 mg, 0.4 mmol) and ethylazidoformate (0.45 g, 3.9 mmol) in a quartz n.m.r. tube was irradiated by a 125W medium pressure mercury lamp for 24 h. During this period small bubbles of nitrogen were observed in the solution. After the photolysis the resulting gum was dissolved in CDCl₃ and the ¹H-n.m.r. spectrum showed that the double bond of the alkene was still present and that no aziridine peak had formed.

f. Attempted reaction with 1-ethoxy-2-(2-dinitroanilino)-1,2,3,4-tetrahydroisoquinoline

A solution of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (39 mg, 0.17 mmol) and 1-ethoxy-2-(2,4-dinitroanilino)-1,2,3,4-tetrahydroisoquinoline (61 mg, 0.17 mmol) in A.R.toluene (6 ml) was heated under reflux for 16 h. On cooling crystals were formed which were filtered off to give the hexahydrotetrazine (26 mg, 0.09 mmol) formed by dimerisation of the 1,3-dipole, m.p. 154-155°C (lit.,⁶⁸ 151-152°C). Evaporation of the filtrate gave a yellow solid (65 mg) whose ¹H-n.m.r. spectrum showed only the dipole dimer and the starting alkene to be present.

g. Attempted reaction with diphenyl nitrile imine

A solution of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (127 mg, 0.55 mmol) and diphenylhydrazidoyl chloride (126 mg, 0.55 mmol) in toluene (5 ml) was heated under reflux for 24 h. T.l.c. on alumina with ether as eluant showed that the starting alkene was unreacted. The solvent

was evaporated and the ^1H -n.m.r. spectrum of the residue confirmed that no reaction had occurred.

4. Preparation and FVP of Diels-Alder Cycloadducts

a. Preparation of 4,5,6,7-tetraphenyl-15-oxo-11,12:13,14-dibenzopentacyclo[8.2.2.1.0^{2,9}0^{3,8}]tetradeca-5,11,13-triene

7,8:9,10-Dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (118 mg, 0.49 mmol) was added to a solution of 1,2,3,4-tetraphenylcyclopentadienone (197 mg, 0.51 mmol) in A.R. toluene (20 ml) and heated under reflux for 42 h. The solvent was evaporated to give a pink-white solid, extraction of this solid with ether removed the unreacted tetraphenylcyclopentadienone to produce a white solid. Due to the insolubility of the product it was sublimed (240°C, 37×10^{-3} mmHg) to give 4,5,6,7-tetraphenyl-15-oxo-11,12:13,14-dibenzopentacyclo[8.2.2.1.0^{2,9}0^{3,8}]tetradeca-5,11,13-triene (197 mg, 63%) as colourless crystals m.p. 263-264°C (Found: C, 91.75; H, 5.5. $\text{C}_{47}\text{H}_{34}\text{O}$ requires C, 91.85; H, 5.6%); ν_{max} 1780 (C=O): no ^1H -n.m.r. obtained; m/z 614 (M^+ , 0.5%), 586 (17), 408 (100), 382 (100) and 178 (100).

b. FVP of 4,5,6,7-tetraphenyl-15-oxo-11,12:13,14-dibenzopentacyclo[8.2.2.1.0^{2,9}0^{3,8}]tetradeca-5,11,13-triene

FVP of the title compound (38 mg, 350°C, 4×10^{-3} mmHg, inlet 230°C) gave a white solid at the exit of the furnace. The ^1H -n.m.r. spectrum suggested that the starting material was not present and the i.r. spectrum showed no carbonyl peak. The compound was recrystallised from benzene to give 4,5,6,7-

tetraphenyl-11,12:13,14-dibenzopentacyclo[8.2.2.0^{2,9}_{0³};7⁰_{0⁴},8⁰]-tetradeca-6,11,13-triene (30 mg, 83%) as clusters of colourless prisms, m.p. 149-151°C; δ_{H} (80MHz; CDCl_3) 2.40-2.53 (2H, m, C(2)H and C(9)H), 3.23 (1H, dd, J 3.7 and 7.5Hz, C(2)H), 3.92-4.00 (2H, m, C(1)H and C(10)H), 4.53 (1H, d, J 3.6Hz, C(7)H) and 6.20-7.31 (24H, m, Ar); m/z 586 (M^+ , 1%) 440 (26), 408 (49), 335 (35), 178 (100), 105 (99) and 77 (39).

An unidentifiable peak at m/z 628(2) was also observed. δ_{C} (50MHz; CDCl_3) 44.58, 44.93, 49.66, 56.96, 59.56, 61.30 (aliphatic carbons), 122.90, 123.80, 124.27, 124.47, 125.54, 126.52, 127.08, 127.47, 128.13, 128.74, 129.07, 129.81, 130.40, 138.10, 142.11 (olefinic and aromatic carbons).

c. Preparation of 4,7-diphenyl-15-oxa-5,6:11,12:13,14-tribenzopentacyclo[8.2.2.1.0^{2,9}_{0³},8⁰]-pentadeca-5,11,13-triene

1,3-Diphenylisobenzofuran (220 mg, 0.81 mmol) was added to a solution of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (188 mg, 0.82 mmol) in dry toluene (25 ml) and heated under reflux for 40 h. The reaction was monitored by t.l.c. on silica gel with ether/*n*-hexane (60:40) as eluant until it showed that no starting alkene was present in the reaction mixture. The solvent was evaporated to give a yellow oil which was triturated with a mixture of ether/ethanol (1:1) to give a yellow solid. Recrystallisation from ethanol removed the unreacted 1,3-diphenylisobenzofuran to give 4,7-diphenyl-15-oxa-5,6:11,12:13,14-tribenzopentacyclo[8.2.2.1.0^{2,9}_{0³},8⁰]-pentadeca-5,11,13-triene (257 mg, 53%) as colourless crystals, m.p. 264-265°C (Found: C, 91.4; H, 5.5. $\text{C}_{38}\text{H}_{28}\text{O}$ requires C, 91.2%; H, 5.65%); ν_{max} 1600 cm^{-1} (C=C); δ_{H} (200MHz; CDCl_3) 2.06-2.09 (2H, m, C(2 or 3)H and C(8 or 9)H), 2.15-2.17 (2H, m,

C(2 or 3)H and C(8 or 9)H), 4.19 (2H, t, J 2.0Hz, C(1)H and C(10)H) and 6.80-7.63 (22H, m, Ar); m/z 500 (M^+ , 5%), 322 (26), 283 (30), 270 (100), 178 (97), 165 (39), 105 (42), and 77 (49).

d. FVP of 4,7-diphenyl-15-oxa-5,6:11,12:13,14-tribenzopentacyclo[8.2.2.1.0^{2,9}3,8]pentadeca-5,11,13-triene

FVP of the title compound (30 mg, 550°C, 6×10^{-3} mmHg, inlet 180°C) gave a yellow liquid (26 mg) at the exit of the furnace. The ^1H -n.m.r. spectrum of the compound showed that 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene and 7,8:9,10-dibenzobicyclo[4.2.2]deca-2,4,7,9-tetraene were present. The other compound which was present could not be identified from the ^1H -n.m.r. spectrum. The products were separated by preparative t.l.c. on alumina with Pet-ether (40-60)-ether (1:1) as the eluant. The more mobile compound, of the two bands which were separated, was yellow but when left overnight in the extraction mixture the solution became clear. The mass spectrum of this compound showed a peak, m/z 286, which was shown to be o-dibenzoylbenzene (15mg). The slower running compound was shown by its ^1H -n.m.r. spectrum to be 7,8:9,10-dibenzobicyclo[4.2.2]deca-2,4,7,9-tetraene (6mg).

e. Preparation of 4,5,6,7-tetrachloro-11,12:13,14-dibenzo-tetracyclo[8.2.2.0^{2,9}3,8]tetradeca-4,6,11,13-tetraene

A solution of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (250 mg, 1.09 mmol) and tetrachlorothiophen-1,1-dioxide in dry benzene (5 ml) was heated under reflux for 48 h, with periodic observation of the reaction by t.l.c. on alumina

with ether as the eluant. Evaporation of the benzene afforded a yellow oil which was triturated with ethanol to give a white solid. Recrystallisation of the solid from ethanol gave 4,5,6,7-tetrachloro-11,12:13,14-dibenzotetracyclo[8.2.2.0^{2,9}-0^{3,8}]tetradeca-4,6,11,13-tetraene (305 mg, 67%) as colourless needles, m.p. 209-210°C (Found: C, 63.1; H, 3.35. $C_{22}H_{14}Cl_4$ requires C, 62.85; H, 3.35%); δ_H (100MHz; $CDCl_3$) 2.38-2.51 (2H, m, C(2)H and C(9)H), 2.75-2.90 (2H, m, C(3)H and C(8)H), 4.39 (2H, t, J 3Hz, C(1)H and C(10)H) and 6.98-7.50 (8H, m, Ar); m/z (only ^{35}Cl peaks listed) 416 (M^+ , 3%), 383 (1), 348 (<1), 312 (<1), 276 (1), 216 (2), 204 (100), 192 (2) and 178 (20).

f. FVP of 4,5,6,7-tetrachloro-11,12:13,14-dibenzotetracyclo[8.2.2.0^{2,9}-0^{3,8}]tetradeca-4,6,11,13-tetraene

FVP of the title compound (17 mg, 600°C, 7×10^{-3} mmHg, inlet 170°C), with a 2 cm length of silica wool packing in the furnace tube to increase the contact time, gave a yellow oil and a white solid (14 mg total mass, 82%) at the exit of the furnace. Analysis by g.l.c. on a 5% SE30 column at 110°C showed the presence of three major components. Comparison of these components with authentics on the g.l.c. showed that the three compounds present were anthracene (36%), dibenzobarrelene (14%) and 1,2,3,4-tetrachlorobenzene (50%). (The percentage yields of the total mass of the products were based on calibration from the 1H -n.m.r. spectrum).

g. Attempted reaction with thiophen-1,1-dioxide

The thiophen-1,1-dioxide was prepared by the method of

Leaver.⁷⁶

Powdered sodium hydroxide (3.0 g, 75 mmol) was added in a single portion to a stirred solution of dibromosulpholane (1.34 g, 4.9 mmol) in dry tetrahydrofuran (70 ml) at 0°C under a nitrogen atmosphere. After 2 h a further portion of sodium hydroxide (3.0 g, 75 mmol) was added to the purple-grey solution. After a total of 3.5 h the solution was filtered through celite under a nitrogen atmosphere and the 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (100 mg, 0.43 mmol) was added. (According to Leaver's u.v. study of this reaction the concentration is maximum after 3.5 h and thereafter decreases, due to dimerisation⁷⁶).

The reaction was stirred for 60 h and the solvent was removed to give a yellow oil. Traces of tetrahydrofuran were removed at 0.05 mmHg to give a yellow semi-solid (1.4g). The t.l.c. on alumina with ether as eluant showed three or more compounds to be present with a significant amount of decomposition on the plate. The ¹H-n.m.r. spectrum showed that the starting alkene had not reacted.

h. FVP of 5-phenyl-4-oxo-10,11:12,13-dibenzotetracyclo-[7.2.2.0^{2,8}0^{3,7}]trideca-5,10,12-triene

The title compound was obtained from Dr. D.C. Billington of Strathclyde University.

FVP of the title compound (30 mg, 650°C, 7×10^{-3} mmHg, inlet 160-180°C) gave a white solid (11 mg) at the exit of the furnace. The ¹H-n.m.r. spectrum showed the presence of only aromatic protons and indicated that one of the compounds was anthracene. T.l.c. on silica gel with ether as eluant showed

that only two compounds were present. Analysis by the g.l.c. on 5% SE30 at 150°C confirmed that two compounds were present and by comparison with authentic samples one component was identified as anthracene (6 mg). The g.l.c.-m.s. showed that the other component had a parent peak, m/z 154 which strongly suggested biphenyl. Comparison with an authentic sample of biphenyl on the g.l.c. confirmed that the other product was biphenyl (5 mg).

E. Preparation and FVP of 5,6:7,8-Dibenzobicyclo[2.2.2]-octa-2,5,7-triene and Derivatives

1. Preparation and FVP of 5,6:7,8-dibenzobicyclo[2.2.2]-octa-2,5,7-triene

a. Attempted preparation of 5,6:7,8-dibenzobicyclo[2.2.2]-octa-2,5,7-triene

(i) 3,5-Dioxo-4-oxa-8,9:10,11-dibenzotricyclo[5.2.2.0^{2,6}]-undeca-8,10-diene

A solution of anthracene (30 g, 168 mmol) and maleic anhydride (16.5 g, 168 mmol) in dry toluene (500 ml) was heated under reflux for 120 h. The solvent was evaporated and the ¹H-n.m.r. spectrum of the remaining white solid showed that the reaction was complete. The crude product was used in the following stage.

(ii) 5,6:7,8-Dibenzobicyclo[2.2.2]octa-5,7-diene-2,3-dicarboxylic acid

The anhydride (46.5 g, 168 mmol) obtained from the foregoing section was added to aqueous sodium hydroxide (1M, 150 ml) and heated under reflux for 2 h. The hot alkaline solution was filtered to remove unreacted anthracene and the filtrate was allowed to cool and acidified with hydrochloric acid (4M) to pH2 to give a white suspension. The solid was filtered off, washed with water, dried under vacuum, crushed and finally dried in a heating pistol to give 5,6:7,8-dibenzobicyclo[2.2.2]-octa-5,7-diene-2,3-dicarboxylic acid (32.6 g, 66%) m.p. 249-

251°C (lit,³⁷ 251-253°C).

(iii) Attempted preparation of 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene using lead tetraacetate

A solution of 5,6:7,8-dibenzobicyclo[2.2.2]octa-5,7-diene-2,3-dicarboxylic acid (18 g, 61 mmol) in dry pyridine (125 ml) was oxygenated by bubbling oxygen through the solution for 20 min. Lead tetraacetate (vacuum dried, 41 g, 93 mmol) was added to the solution in one portion and the mixture was heated to 68°C for 8 min. (A vigorous effervescence of carbon dioxide was observed during this period as the solution changed colour from orange to brown). The warm reaction mixture was poured into 10% nitric acid (2000 ml) and extracted with dichloromethane (4 x 250 ml). The organic extract was washed with aqueous sodium hydrogen carbonate and water, dried and the solvent was evaporated to give a pale yellow solid. The ¹H-n.m.r. spectrum of the crude material showed that the diacid had formed the anhydride. Chromatography on silica gel with Pet.ether (40-60) as eluant gave an unidentified product (76 mg) whose ¹H-n.m.r. spectrum showed that this was not the desired compound.

(iv) Preparation of 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene using dicarbonyl-bis(triphenylphosphine) nickel

The method of Dauben⁷⁷ was used in this preparation.

A solution of 5,6:7,8-dibenzobicyclo[2.2.2]octa-5,7-diene-2,3-dicarboxylic acid (0.984 g, 3.56 mmol) and dicarbonyl-bis(triphenylphosphine) nickel (2.482 g, 3.88 mmol) in anhydrous diglyme (10 ml) was heated under vigorous reflux, in a nitrogen atmosphere, for 210 min. The solution was cooled, poured into

water (120 ml) and extracted with *n*-hexane (4 x 50 ml). The solution was dried and the *n*-hexane was evaporated to give a yellow solution of diglyme and product. The diglyme was evaporated at 0.05 mmHg to give a yellow oil which crystallised on standing. Chromatography on silica gel with Pet-ether (40-60)-ether (85:15) as eluant gave triphenylphosphine m.p. 76°C (lit., 79-81°C) firstly. The second compound eluted had a ¹H-n.m.r. spectrum which showed it to be the desired alkene (87 mg, 12%) m.p. 119-120°C (lit.,⁷⁷ 119-120.5°C).

b. Preparation of 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene

This method was based on that of H.P. Figeys.⁴

(i) Dimethyl-5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylate

Prepared by the method of Diels and Alder.³⁷

Anthracene (10.0 g, 56.2 mmol) was added to neat dimethyl acetylene dicarboxylate (9.8 ml, 79.8 mmol) and the mixture was heated to 160°C. At this temperature addition occurred to give a brown fluid which gave a yellow crystalline solid on cooling to 20°C. Recrystallisation from methanol gave dimethyl 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylate (13.7 g, 76%) as off white crystals m.p. 160-161°C (lit.,³⁷ 160-161°C).

(ii) 5,6:7,8-Dibenzobicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylic acid

A solution of dimethyl 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylate (13.7 g, 42.8 mmol) in 2N

sodium hydroxide (120 ml) and methanol (60 ml) was heated under reflux for 1 h. After cooling the mixture was acidified with 4M hydrochloric acid to produce a white precipitate. The precipitate was filtered off to give a white solid which was washed with water and dried in a drying pistol to give 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylic acid (11.9 g, 95%) as colourless crystals m.p. 215-216°C (lit.⁴ 215.5-216°C).

(iii) 5,6:7,8-Dibenzobicyclo[2.2.2]octa-2,5⁷-triene

Copper powder (1.443 g, 22.7 mmol) was added to a solution of 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylic acid (8.15 g, 27.9 mmol) in quinoline (16 ml) and the mixture was heated under reflux for 150 min (20 min after gas evolution had ceased). The solution was cooled, diluted with chloroform and filtered, the copper powder was washed repeatedly with chloroform until the organic washings were colourless. The combined organic fractions were successively washed with 10% aqueous sodium hydroxide, water, 10% aqueous hydrochloric acid and finally water. The organic phase was dried and the solvent was evaporated. Chromatography of the residue on silica gel with Pet:ether (40-60) as the eluant gave anthracene (0.65 g) as the first eluted compound, due to the retro-Diels-Alder reaction. The second compound to be eluted was a white crystalline compound which was recrystallised from ethanol to give 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene (2.30 g, 40%) as colourless crystals m.p. 119-120°C (lit.⁷⁸ 119-120.5°C).

c. FVP of 5,6:7,8-Dibenzobicyclo[2.2.2]octa-2,5,7-triene

FVP of the title compound (100 mg, 750°C, 5×10^{-3} mmHg, inlet 80°C (minimum temperature possible)) gave a white solid (75 mg, 75%) at the exit whose ^1H -n.m.r. spectrum showed it to be a mixture of starting material and anthracene. Analysis by the g.l.c. on 5% SE30 at 170°C determined the yields of the starting material (68%) and anthracene (32%).

2. Reaction with 1,3-dipoles and FVP of adducts

a. Preparation of 5-phenyl-3-oxa-4-aza-8,9:10,11-dibenzotricyclo[5.2.2.0^{2,6}]undec-4,8,10-triene

A solution of 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene (200 mg, 0.98 mmol) and benzohydroximoyl chloride (180 mg, 1.09 mmol) in toluene (25 ml) was heated under reflux for 75 h (during this period the colour of the solution changed from colourless to yellow). The reaction was monitored by the disappearance of the starting alkene by t.l.c. on alumina with Pet.ether (40-60) as eluant. The toluene was evaporated to give a yellow oil which was triturated with ethanol to give a pale yellow solid. Recrystallisation from ethanol gave 5-phenyl-3-oxa-4-aza-8,9:10,11-dibenzotricyclo[5.2.2.0^{2,6}]undec-4,8,10-triene (205 mg, 64%) as pale yellow crystals m.p. 153-155°C (Found: C, 85.35; H, 5.3; N, 4.3. $\text{C}_{23}\text{H}_{17}\text{NO}$ requires C, 85.4; H, 5.3; N, 4.35%); δ_{H} (80MHz, CDCl_3) 4.30 (1H, dd, J 10.1 and 3.3Hz, C(6)H) 4.58 (1H, d, J 3.6 C(1)H or C(7)H) 4.74 (1H, d, J 3.6Hz, C(1)H or C(7)H), 5.25 (1H, dd, J 10.3 and 3.6Hz,

C(2)H) and 6.68-7.56 (13H, m, Ar); m/z 323 (M^+ , <1%) and 178 (100).

b. FVP of 5-phenyl-3-oxa-4-aza-8,9:10,11-dibenzotricyclo-[5.2.2.0^{2,6}]undec-4,8,10-triene

FVP of the title compound (41 mg, 350°C, 7×10^{-3} mmHg, inlet 125-130°C) gave a pale yellow solid (29 mg, 71%) at the exit of the furnace. Preparative t.l.c. on silica gel with Pet.ether (40-60) as eluant separated two products which were present and gave anthracene (16mg) which was identified by its ^1H -n.m.r. spectrum, and another compound (8mg). The ^1H n.m.r.spectrum of the other compound suggested that it was 3-phenylisoxazole δ_{H} (80MHz; CDCl_3) 6.65 (1H, d, J 2Hz, C(4)H), 7.36-7.55 (5H, m, Ph) and 7.7-7.9 (1H, peak obscured due to contaminant anthracene). The analysis by g.l.c. on 5% SE30 at 170°C showed that the 3-phenylisoxazole was 95% pure, contaminated with anthracene (3%) and starting material (2%). The g.l.c.-m.s. of the product gave a parent peak m/z 145 which confirmed that the compound was 3-phenylisoxazole.

c. Attempted reaction with 1-piperidine^e-1-oxide

1-Piperidine^e-1-oxide (121 mg, 1.22 mmol) was added to a stirred solution of 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene (240 mg, 1.18 mmol) in toluene (10 ml) and the mixture was heated under reflux for 13 h. T.l.c. showed that the alkene had not reacted but the solution had darkened in colour. The solvent was evaporated to afford a brown gum whose ^1H -n.m.r. spectrum showed the unreacted starting alkene to be the main compound present.

d. Preparation of 3-*N*-carbethoxy-6,7:8,9-dibenzotricyclo[2.2.2.0^{2,4}]nona-6,8-diene

A solution of 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene (208 mg, 1.02 mmol) in ethyl azidoformate (1.5 g, 13.0 mmol) in a quartz n.m.r. tube was irradiated by a 125W medium pressure photochemical lamp for 4 h. Chromatography of the crude mixture on alumina with ether as eluant gave a white solid. Recrystallisation of the solid from ethanol gave 3-*N*-carbethoxy-6,7:8,9-dibenzotricyclo[2.2.2.0^{2,4}]nona-6,8-diene (115 mg, 39%) as colourless needles, m.p. 189-191°C (Found: C, 78.2; H, 5.7; N, 4.75. C₁₉H₁₇NO₂ requires C, 78.3; H, 5.9; N, 4.8%); ν_{\max} 1715 cm⁻¹ (C=O); δ_{H} (80MHz; CDCl₃) 1.18 (3H, t, J 7.0Hz, CH₃), 3.15 (2H, dd, J 2.9 and 1.9Hz, C(2)H and C(4)H), 4.00 (2H, q, J 7.1Hz, CH₂) 4.65 (2H, dd, J 2.7 and 2.0Hz, C(1)H and C(5)H) and 7.02-7.38 (8H, m, Ar); m/z 291 (M⁺, 57%), 246 (9), 218 (18), 202 (59), 191 (100) and 178 (20).

e. FVP of 3-*N*-carbethoxy-6,7:8,9-dibenzotricyclo[2.2.2.0^{2,4}]nona-6,8-diene

FVP of the title compound (22 mg, 600°C, 7 x 10⁻³ mmHg, inlet 135°C) gave a white solid (11 mg) at the exit of the furnace, whose ¹H-n.m.r. spectrum showed it to be anthracene, and a yellow fluorescent liquid in the trap at the liquid nitrogen level. Preparative t.l.c. on alumina with ether as eluant gave anthracene (4mg) and a compound at R_f 0.3 (4 mg). The ¹H-n.m.r. of the compound at R_f 0.3 showed the presence of an aldehyde proton at δ 9.95. The mass spectrum of the compound at R_f 0.3

contained at large peak at 220 (Found: M^+ 220.092009. $C_{16}H_{12}O$ requires 220.088810). This compound was identified as 3,4:6,7-dibenzocycloheptene-5-carboxaldehyde or 3,4:6,7-dibenzocycloheptene-1-carboxaldehyde.

f. Attempted reaction with *p*-anisonitrile sulphide

A solution of 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene (204 mg, 1.0 mmol) and 5-(*p*-methoxyphenyl)-[1,3,4]-oxathiazol-2-one (207 mg, 0.99 mmol) in toluene (13 ml) was heated under reflux for 64 h. The t.l.c. during the reaction showed the presence of a new compound. Evaporation of the solvent yielded a brown oil which was chromatographed by preparative t.l.c. on silica gel with ether-Pet.ether (40:60) (1:2) as eluant to give two compounds. The 1H -n.m.r. spectrum of the faster running compound showed that it was anthracene (160mg). The 1H -n.m.r. of the slower compound suggested that it was the dipole precursor but the i.r. spectrum ν_{max} 2220 cm^{-1} (nitrile) revealed that the dipole had been generated but decomposed to give the nitrile (147 mg).

3. Preparation and FVP of Diels Alder cycloadducts

a. Attempted reaction with 1,2,3,4-tetraphenylcyclopentadienone

A solution of 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene (330 mg, 1.62 mmol) and 1,2,3,4-tetraphenylcyclopentadienone (621 mg, 1.62 mmol) in toluene (15 ml) was heated under reflux for 64 h. Examination by t.l.c. showed that no reaction had taken place. The solvent was evaporated and the

^1H -n.m.r. spectrum showed that the starting alkene was still present. Preparative t.l.c. on alumina using *n*-hexane/ether (9:1) as eluant recovered the 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene (300 mg).

The reaction was repeated using xylene instead of toluene but the ^1H n.m.r. spectrum showed that no reaction had occurred.

b. Preparation of 3,6-diphenyl-13-oxa-4,5:9,10:11,12-tribenzotetracyclo[6.2.2.1.0^{2,7}]trideca-4,9,11-triene

A solution of 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene (204 mg, 1.00 mmol) and 1,3-diphenylisobenzofuran (283 mg, 1.05 mmol) in toluene (20 ml) was heated under reflux for 20 h. (During this period the colour of the solution changed from yellow to colourless). The solvent was evaporated to give a white solid. Recrystallisation from ethanol gave 3,6-diphenyl-13-oxa-4,5:9,10:11,12-tribenzotetracyclo[6.2.2.1.0^{2,7}]trideca-4,9,11-triene (317 mg, 67%) as colourless crystals m.p. 255-256°C, decomposes with colour change from colourless to yellow, (Found: C, 90.9; H, 5.45. $\text{C}_{38}\text{H}_{26}\text{O}$ requires C, 91.1; H, 5.55%); δ_{H} (80MHz; CDCl_3) 2.89 (2H, t, J 1.2Hz, C(2)H and C(7)H), 4.15 (2H, br s, C(1)H and C(8)H), 6.81-7.25 (12H, m, Ar) and 7.48 (10H, s, Ph); m/z 474 (M^+ , <0.1%), 283 (47), 270 (100), 241 (11) and 178 (14).

c. FVP of 3,6-diphenyl-13-oxa-4,5:9,10:11,12-tribenzotetracyclo[6.2.2.1.0^{2,7}]trideca-4,9,11-triene

FVP of the title compound (16 mg, 500°C, 6×10^{-3} mmHg, inlet 120-145°C) gave a yellow solid (13 mg, 81%) at the exit of the furnace, which became a colourless oil after contact with

air for 10 h. The ^1H -n.m.r. spectrum of the liquid showed that 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene was one of the compounds present and that the remaining compounds had only aromatic protons. The mass spectrum of the crude products showed peaks at 286 and 204. The peak at 286 was identified as o-dibenzoylbenzene. G.l.c. of the crude product only gave one identifiable compound on SE30 at 170°C and this was found to be 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene (24%).

d. Preparation of 3,4,5,6-tetrachloro-9,10:11,12-dibenzotricyclo[6.2.2.0^{2,7}]dodeca-3,5,9,11-tetraene

A solution of 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene (398 mg, 1.95 mmol) and tetrachlorothiophen-1,1-dioxide (469 mg, 1.95 mmol) in toluene (25 ml) was heated under reflux for 18 h to give a light brown solution. T.l.c. on alumina with ether as eluant showed that the starting alkene had disappeared. The toluene was evaporated and the residual brown gum was triturated with ethanol to yield light brown crystals. Recrystallisation gave 3,4,5,6-tetrachloro-9,10:11,12-dibenzotricyclo[6.2.2.0^{2,7}]dodeca-3,5,9,11-tetraene (483 mg, 63%) as colourless rhombic plates m.p. $278-280^\circ\text{C}$, with decomposition, (Found: C, 52.35; H, 2.5. $\text{C}_{20}\text{H}_{12}\text{Cl}_4$ requires C, 52.4; H, 2.65%); δ_{H} (80MHz; CDCl_3) 4.86 (2H, s, C(1)H and C(8)H), 5.00 (2H, s, C(2)H and C(7)H) and 7.17-7.49 (8H, m, Ar); m/z 430 (M^+ , 4%), 296 (30), 226 (45) and 178 (100).

e. FVP of 3,4,5,6-tetrachloro-9,10:11,12-dibenzotricyclo-
[6.2.2.0^{2,7}]dodeca-3,5,9,11-tetraene

FVP of the title compound (29 mg, 580°C, 6×10^{-3} mmHg, inlet 210°C) gave a white solid at the exit of the furnace and a pale yellow solid at the liquid nitrogen level of the trap. The ¹H-n.m.r. spectrum of the white solid showed it to be anthracene. The ¹H-n.m.r. spectrum of the yellow solid showed only a small quantity of anthracene, however the tetrachlorobenzene peak, δ_H 7.22, may have been hidden under the chloroform peak, δ_H 7.28. The two solids were analysed by g.c. on 5% SE30 at 170°C and showed that two components were present. Comparison with authentic samples by g.l.c. showed that 1,2,3,4-tetrachlorobenzene (15 mg) and anthracene (12 mg) were present.

f. FVP of 1,3-diphenylisobenzofuran

FVP of 1,3-diphenylisobenzofuran (50 mg, 650°C, 6×10^{-3} mmHg, inlet 140°C) gave a yellow fluorescent solid (43 mg) at the exit of the furnace. After the product was dissolved in CDCl₃ and kept at room temperature for 4 h the solution remained unchanged. The ¹H-n.m.r. spectrum of the compound showed only aromatic protons to be present and the compound to be starting material. δ_H 7.22, 7.28, 7.32, 7.38, 7.42, 7.48, 7.52, 7.58, 7.62, 7.68, 7.72, 7.78, 7.82, 7.88, 7.92, 7.98, 8.02, 8.08, 8.12, 8.18, 8.22, 8.28, 8.32, 8.38, 8.42, 8.48, 8.52, 8.58, 8.62, 8.68, 8.72, 8.78, 8.82, 8.88, 8.92, 8.98, 9.02, 9.08, 9.12, 9.18, 9.22, 9.28, 9.32, 9.38, 9.42, 9.48, 9.52, 9.58, 9.62, 9.68, 9.72, 9.78, 9.82, 9.88, 9.92, 9.98, 10.02, 10.08, 10.12, 10.18, 10.22, 10.28, 10.32, 10.38, 10.42, 10.48, 10.52, 10.58, 10.62, 10.68, 10.72, 10.78, 10.82, 10.88, 10.92, 10.98, 11.02, 11.08, 11.12, 11.18, 11.22, 11.28, 11.32, 11.38, 11.42, 11.48, 11.52, 11.58, 11.62, 11.68, 11.72, 11.78, 11.82, 11.88, 11.92, 11.98, 12.02, 12.08, 12.12, 12.18, 12.22, 12.28, 12.32, 12.38, 12.42, 12.48, 12.52, 12.58, 12.62, 12.68, 12.72, 12.78, 12.82, 12.88, 12.92, 12.98, 13.02, 13.08, 13.12, 13.18, 13.22, 13.28, 13.32, 13.38, 13.42, 13.48, 13.52, 13.58, 13.62, 13.68, 13.72, 13.78, 13.82, 13.88, 13.92, 13.98, 14.02, 14.08, 14.12, 14.18, 14.22, 14.28, 14.32, 14.38, 14.42, 14.48, 14.52, 14.58, 14.62, 14.68, 14.72, 14.78, 14.82, 14.88, 14.92, 14.98, 15.02, 15.08, 15.12, 15.18, 15.22, 15.28, 15.32, 15.38, 15.42, 15.48, 15.52, 15.58, 15.62, 15.68, 15.72, 15.78, 15.82, 15.88, 15.92, 15.98, 16.02, 16.08, 16.12, 16.18, 16.22, 16.28, 16.32, 16.38, 16.42, 16.48, 16.52, 16.58, 16.62, 16.68, 16.72, 16.78, 16.82, 16.88, 16.92, 16.98, 17.02, 17.08, 17.12, 17.18, 17.22, 17.28, 17.32, 17.38, 17.42, 17.48, 17.52, 17.58, 17.62, 17.68, 17.72, 17.78, 17.82, 17.88, 17.92, 17.98, 18.02, 18.08, 18.12, 18.18, 18.22, 18.28, 18.32, 18.38, 18.42, 18.48, 18.52, 18.58, 18.62, 18.68, 18.72, 18.78, 18.82, 18.88, 18.92, 18.98, 19.02, 19.08, 19.12, 19.18, 19.22, 19.28, 19.32, 19.38, 19.42, 19.48, 19.52, 19.58, 19.62, 19.68, 19.72, 19.78, 19.82, 19.88, 19.92, 19.98, 20.02, 20.08, 20.12, 20.18, 20.22, 20.28, 20.32, 20.38, 20.42, 20.48, 20.52, 20.58, 20.62, 20.68, 20.72, 20.78, 20.82, 20.88, 20.92, 20.98, 21.02, 21.08, 21.12, 21.18, 21.22, 21.28, 21.32, 21.38, 21.42, 21.48, 21.52, 21.58, 21.62, 21.68, 21.72, 21.78, 21.82, 21.88, 21.92, 21.98, 22.02, 22.08, 22.12, 22.18, 22.22, 22.28, 22.32, 22.38, 22.42, 22.48, 22.52, 22.58, 22.62, 22.68, 22.72, 22.78, 22.82, 22.88, 22.92, 22.98, 23.02, 23.08, 23.12, 23.18, 23.22, 23.28, 23.32, 23.38, 23.42, 23.48, 23.52, 23.58, 23.62, 23.68, 23.72, 23.78, 23.82, 23.88, 23.92, 23.98, 24.02, 24.08, 24.12, 24.18, 24.22, 24.28, 24.32, 24.38, 24.42, 24.48, 24.52, 24.58, 24.62, 24.68, 24.72, 24.78, 24.82, 24.88, 24.92, 24.98, 25.02, 25.08, 25.12, 25.18, 25.22, 25.28, 25.32, 25.38, 25.42, 25.48, 25.52, 25.58, 25.62, 25.68, 25.72, 25.78, 25.82, 25.88, 25.92, 25.98, 26.02, 26.08, 26.12, 26.18, 26.22, 26.28, 26.32, 26.38, 26.42, 26.48, 26.52, 26.58, 26.62, 26.68, 26.72, 26.78, 26.82, 26.88, 26.92, 26.98, 27.02, 27.08, 27.12, 27.18, 27.22, 27.28, 27.32, 27.38, 27.42, 27.48, 27.52, 27.58, 27.62, 27.68, 27.72, 27.78, 27.82, 27.88, 27.92, 27.98, 28.02, 28.08, 28.12, 28.18, 28.22, 28.28, 28.32, 28.38, 28.42, 28.48, 28.52, 28.58, 28.62, 28.68, 28.72, 28.78, 28.82, 28.88, 28.92, 28.98, 29.02, 29.08, 29.12, 29.18, 29.22, 29.28, 29.32, 29.38, 29.42, 29.48, 29.52, 29.58, 29.62, 29.68, 29.72, 29.78, 29.82, 29.88, 29.92, 29.98, 30.02, 30.08, 30.12, 30.18, 30.22, 30.28, 30.32, 30.38, 30.42, 30.48, 30.52, 30.58, 30.62, 30.68, 30.72, 30.78, 30.82, 30.88, 30.92, 30.98, 31.02, 31.08, 31.12, 31.18, 31.22, 31.28, 31.32, 31.38, 31.42, 31.48, 31.52, 31.58, 31.62, 31.68, 31.72, 31.78, 31.82, 31.88, 31.92, 31.98, 32.02, 32.08, 32.12, 32.18, 32.22, 32.28, 32.32, 32.38, 32.42, 32.48, 32.52, 32.58, 32.62, 32.68, 32.72, 32.78, 32.82, 32.88, 32.92, 32.98, 33.02, 33.08, 33.12, 33.18, 33.22, 33.28, 33.32, 33.38, 33.42, 33.48, 33.52, 33.58, 33.62, 33.68, 33.72, 33.78, 33.82, 33.88, 33.92, 33.98, 34.02, 34.08, 34.12, 34.18, 34.22, 34.28, 34.32, 34.38, 34.42, 34.48, 34.52, 34.58, 34.62, 34.68, 34.72, 34.78, 34.82, 34.88, 34.92, 34.98, 35.02, 35.08, 35.12, 35.18, 35.22, 35.28, 35.32, 35.38, 35.42, 35.48, 35.52, 35.58, 35.62, 35.68, 35.72, 35.78, 35.82, 35.88, 35.92, 35.98, 36.02, 36.08, 36.12, 36.18, 36.22, 36.28, 36.32, 36.38, 36.42, 36.48, 36.52, 36.58, 36.62, 36.68, 36.72, 36.78, 36.82, 36.88, 36.92, 36.98, 37.02, 37.08, 37.12, 37.18, 37.22, 37.28, 37.32, 37.38, 37.42, 37.48, 37.52, 37.58, 37.62, 37.68, 37.72, 37.78, 37.82, 37.88, 37.92, 37.98, 38.02, 38.08, 38.12, 38.18, 38.22, 38.28, 38.32, 38.38, 38.42, 38.48, 38.52, 38.58, 38.62, 38.68, 38.72, 38.78, 38.82, 38.88, 38.92, 38.98, 39.02, 39.08, 39.12, 39.18, 39.22, 39.28, 39.32, 39.38, 39.42, 39.48, 39.52, 39.58, 39.62, 39.68, 39.72, 39.78, 39.82, 39.88, 39.92, 39.98, 40.02, 40.08, 40.12, 40.18, 40.22, 40.28, 40.32, 40.38, 40.42, 40.48, 40.52, 40.58, 40.62, 40.68, 40.72, 40.78, 40.82, 40.88, 40.92, 40.98, 41.02, 41.08, 41.12, 41.18, 41.22, 41.28, 41.32, 41.38, 41.42, 41.48, 41.52, 41.58, 41.62, 41.68, 41.72, 41.78, 41.82, 41.88, 41.92, 41.98, 42.02, 42.08, 42.12, 42.18, 42.22, 42.28, 42.32, 42.38, 42.42, 42.48, 42.52, 42.58, 42.62, 42.68, 42.72, 42.78, 42.82, 42.88, 42.92, 42.98, 43.02, 43.08, 43.12, 43.18, 43.22, 43.28, 43.32, 43.38, 43.42, 43.48, 43.52, 43.58, 43.62, 43.68, 43.72, 43.78, 43.82, 43.88, 43.92, 43.98, 44.02, 44.08, 44.12, 44.18, 44.22, 44.28, 44.32, 44.38, 44.42, 44.48, 44.52, 44.58, 44.62, 44.68, 44.72, 44.78, 44.82, 44.88, 44.92, 44.98, 45.02, 45.08, 45.12, 45.18, 45.22, 45.28, 45.32, 45.38, 45.42, 45.48, 45.52, 45.58, 45.62, 45.68, 45.72, 45.78, 45.82, 45.88, 45.92, 45.98, 46.02, 46.08, 46.12, 46.18, 46.22, 46.28, 46.32, 46.38, 46.42, 46.48, 46.52, 46.58, 46.62, 46.68, 46.72, 46.78, 46.82, 46.88, 46.92, 46.98, 47.02, 47.08, 47.12, 47.18, 47.22, 47.28, 47.32, 47.38, 47.42, 47.48, 47.52, 47.58, 47.62, 47.68, 47.72, 47.78, 47.82, 47.88, 47.92, 47.98, 48.02, 48.08, 48.12, 48.18, 48.22, 48.28, 48.32, 48.38, 48.42, 48.48, 48.52, 48.58, 48.62, 48.68, 48.72, 48.78, 48.82, 48.88, 48.92, 48.98, 49.02, 49.08, 49.12, 49.18, 49.22, 49.28, 49.32, 49.38, 49.42, 49.48, 49.52, 49.58, 49.62, 49.68, 49.72, 49.78, 49.82, 49.88, 49.92, 49.98, 50.02, 50.08, 50.12, 50.18, 50.22, 50.28, 50.32, 50.38, 50.42, 50.48, 50.52, 50.58, 50.62, 50.68, 50.72, 50.78, 50.82, 50.88, 50.92, 50.98, 51.02, 51.08, 51.12, 51.18, 51.22, 51.28, 51.32, 51.38, 51.42, 51.48, 51.52, 51.58, 51.62, 51.68, 51.72, 51.78, 51.82, 51.88, 51.92, 51.98, 52.02, 52.08, 52.12, 52.18, 52.22, 52.28, 52.32, 52.38, 52.42, 52.48, 52.52, 52.58, 52.62, 52.68, 52.72, 52.78, 52.82, 52.88, 52.92, 52.98, 53.02, 53.08, 53.12, 53.18, 53.22, 53.28, 53.32, 53.38, 53.42, 53.48, 53.52, 53.58, 53.62, 53.68, 53.72, 53.78, 53.82, 53.88, 53.92, 53.98, 54.02, 54.08, 54.12, 54.18, 54.22, 54.28, 54.32, 54.38, 54.42, 54.48, 54.52, 54.58, 54.62, 54.68, 54.72, 54.78, 54.82, 54.88, 54.92, 54.98, 55.02, 55.08, 55.12, 55.18, 55.22, 55.28, 55.32, 55.38, 55.42, 55.48, 55.52, 55.58, 55.62, 55.68, 55.72, 55.78, 55.82, 55.88, 55.92, 55.98, 56.02, 56.08, 56.12, 56.18, 56.22, 56.28, 56.32, 56.38, 56.42, 56.48, 56.52, 56.58, 56.62, 56.68, 56.72, 56.78, 56.82, 56.88, 56.92, 56.98, 57.02, 57.08, 57.12, 57.18, 57.22, 57.28, 57.32, 57.38, 57.42, 57.48, 57.52, 57.58, 57.62, 57.68, 57.72, 57.78, 57.82, 57.88, 57.92, 57.98, 58.02, 58.08, 58.12, 58.18, 58.22, 58.28, 58.32, 58.38, 58.42, 58.48, 58.52, 58.58, 58.62, 58.68, 58.72, 58.78, 58.82, 58.88, 58.92, 58.98, 59.02, 59.08, 59.12, 59.18, 59.22, 59.28, 59.32, 59.38, 59.42, 59.48, 59.52, 59.58, 59.62, 59.68, 59.72, 59.78, 59.82, 59.88, 59.92, 59.98, 60.02, 60.08, 60.12, 60.18, 60.22, 60.28, 60.32, 60.38, 60.42, 60.48, 60.52, 60.58, 60.62, 60.68, 60.72, 60.78, 60.82, 60.88, 60.92, 60.98, 61.02, 61.08, 61.12, 61.18, 61.22, 61.28, 61.32, 61.38, 61.42, 61.48, 61.52, 61.58, 61.62, 61.68, 61.72, 61.78, 61.82, 61.88, 61.92, 61.98, 62.02, 62.08, 62.12, 62.18, 62.22, 62.28, 62.32, 62.38, 62.42, 62.48, 62.52, 62.58, 62.62, 62.68, 62.72, 62.78, 62.82, 62.88, 62.92, 62.98, 63.02, 63.08, 63.12, 63.18, 63.22, 63.28, 63.32, 63.38, 63.42, 63.48, 63.52, 63.58, 63.62, 63.68, 63.72, 63.78, 63.82, 63.88, 63.92, 63.98, 64.02, 64.08, 64.12, 64.18, 64.22, 64.28, 64.32, 64.38, 64.42, 64.48, 64.52, 64.58, 64.62, 64.68, 64.72, 64.78, 64.82, 64.88, 64.92, 64.98, 65.02, 65.08, 65.12, 65.18, 65.22, 65.28, 65.32, 65.38, 65.42, 65.48, 65.52, 65.58, 65.62, 65.68, 65.72, 65.78, 65.82, 65.88, 65.92, 65.98, 66.02, 66.08, 66.12, 66.18, 66.22, 66.28, 66.32, 66.38, 66.42, 66.48, 66.52, 66.58, 66.62, 66.68, 66.72, 66.78, 66.82, 66.88, 66.92, 66.98, 67.02, 67.08, 67.12, 67.18, 67.22, 67.28, 67.32, 67.38, 67.42, 67.48, 67.52, 67.58, 67.62, 67.68, 67.72, 67.78, 67.82, 67.88, 67.92, 67.98, 68.02, 68.08, 68.12, 68.18, 68.22, 68.28, 68.32, 68.38, 68.42, 68.48, 68.52, 68.58, 68.62, 68.68, 68.72, 68.78, 68.82, 68.88, 68.92, 68.98, 69.02, 69.08, 69.12, 69.18, 69.22, 69.28, 69.32, 69.38, 69.42, 69.48, 69.52, 69.58, 69.62, 69.68, 69.72, 69.78, 69.82, 69.88, 69.92, 69.98, 70.02, 70.08, 70.12, 70.18, 70.22, 70.28, 70.32, 70.38, 70.42, 70.48, 70.52, 70.58, 70.62, 70.68, 70.72, 70.78, 70.82, 70.88, 70.92, 70.98, 71.02, 71.08, 71.12, 71.18, 71.22, 71.28, 71.32, 71.38, 71.42, 71.48, 71.52, 71.58, 71.62, 71.68, 71.72, 71.78, 71.82, 71.88, 71.92, 71.98, 72.02, 72.08, 72.12, 72.18, 72.22, 72.28, 72.32, 72.38, 72.42, 72.48, 72.52, 72.58, 72.62, 72.68, 72.72, 72.78, 72.82, 72.88, 72.92, 72.98, 73.02, 73.08, 73.12, 73.18, 73.22, 73.28, 73.32, 73.38, 73.42, 73.48, 73.52, 73.58, 73.62, 73.68, 73.72, 73.78, 73.82, 73.88, 73.92, 73.98, 74.02, 74.08, 74.12, 74.18, 74.22, 74.28, 74.32, 74.38, 74.42, 74.48, 74.52, 74.58, 74.62, 74.68, 74.72, 74.78, 74.82, 74.88, 74.92, 74.98, 75.02, 75.08, 75.12, 75.18, 75.22, 75.28, 75.32, 75.38, 75.42, 75.48, 75.52, 75.58, 75.62, 75.68, 75.72, 75.78, 75.82, 75.88, 75.92, 75.98, 76.02, 76.08, 76.12, 76.18, 76.22, 76.28, 76.32, 76.38, 76.42, 76.48, 76.52, 76.58, 76.62, 76.68, 76.72, 76.78, 76.82, 76.88, 76.92, 76.98, 77.02, 77.08, 77.12, 77.18, 77.22, 77.28, 77.32, 77.38, 77.42, 77.48, 77.52, 77.58, 77.62, 77.68, 77.72, 77.78, 77.82, 77.88, 77.92, 77.98, 78.02, 78.08, 78.12, 78.18, 78.22, 78.28, 78.32, 78.38, 78.42, 78.48, 78.52, 78.58, 78.62, 78.68, 78.72, 78.78, 78.82, 78.88, 78.92, 78.98, 79.02, 79.08, 79.12, 79.18, 79.22, 79.28, 79.32, 79.38, 79.42, 79.48, 79.52, 79.58, 79.62, 79.68, 79.72, 79.78, 79.82, 79.88, 79.92, 79.98, 80.02, 80.08, 80.12, 80.18, 80.22, 80.28, 80.32, 80.38, 80.42, 80.48, 80.52, 80.58, 80.62, 80.68, 80.72, 80.78, 80.82, 80.88, 80.92, 80.98, 81.02, 81.08, 81.12, 81.18, 81.22, 81.28, 81.32, 81.38, 81.42, 81.48, 81.52, 81.58, 81.62, 81.68, 81.72, 81.78, 81.82, 81.88, 81.92, 81.98, 82.02, 82.08, 82.12, 82.18, 82.22, 82.28, 82.32, 82.38, 82.42, 82.48, 82.52, 82.58, 82.62, 82.68, 82.72, 82.78, 82.82, 82.88, 82.92, 82.98, 83.02, 83.08, 83.12, 83.18, 83.22, 83.28, 83.32, 83.38, 83.42, 83.48, 83.52, 83.58, 83.62, 83.68, 83.72, 83.78, 83.82, 83.88, 83.92, 83.98, 84.02, 84.08, 84.12, 84.18, 84.22, 84.28, 84.32, 84.38, 84.42, 84.48, 84.52, 84.58, 84.62, 84.68, 84.72, 84.78, 84.82, 84.88, 84.92, 84.98, 85.02, 85.08, 85.12, 85.18, 85.22, 85.28, 85.32, 85.38, 85.42, 85.48, 85.52, 85.58, 85.62, 85.68, 85.72, 85.78, 85.82, 85.88, 85.92, 85.98, 86.02, 86.08, 86.12, 86.18, 86.22, 86.28, 86.32, 86.38, 86.42, 86.48, 86.52, 86.58, 86.62, 86.68, 86.72, 86.78, 86.82, 86.88, 86.92, 86.98, 87.02, 87.08, 87.12, 87.18, 87.22, 87.28, 87.32, 87.38, 87.42, 87.48, 87.52, 87.58, 87.62, 87.68, 87.72, 87.78, 87.82, 87.88, 87.92, 87.98, 88.02, 88.08, 88.12, 88.18, 88.22, 88.28, 88.32, 88.38, 88.42, 88.48, 88.52, 88.58, 88.62, 88.68, 88.72, 88.78, 88.82, 88.88, 88.92, 88.98, 89.02, 89.08, 89.12, 89.18, 89.22, 89.28, 89.32, 89.38, 89.42, 89.48, 89.52, 89.58, 89.62, 89.68, 89.72, 89.78, 89.82, 89.88, 89.92, 89.98, 90.02, 90.08, 90.12, 90.18, 90.22, 90.28, 90.32, 90.38, 90.42, 90.48, 90.52, 90.58, 90.62, 90.68, 90.72, 90.78, 90.82, 90.88, 90.92, 90.98, 91.02, 91.08, 91.12, 91.18, 91.22, 91.28, 91.32, 91.38, 91.

F. Polymerisation Reactions of Cyclic Alkenes via Metathesis

1. Polymerisation of bicyclo[2.2.1]hept-2-ene via metathesis

A solution of tetramethyltin (20 mg, 0.11 mmol) chlorobenzene (0.5 ml) and a solution of tungsten hexachloride (20 mg, 0.05 mmol) in chlorobenzene (0.5 ml) were added simultaneously to freshly distilled bicyclo[2.2.1]hept-2-ene (2.00 g, 10.6 mmol) dissolved in dry chlorobenzene (15 ml) under a dry nitrogen atmosphere. The solution was swirled for 15s to allow a homogeneous mixture to form, during this period the mixture became increasingly viscous with a gel forming after 60s. The metathesis was terminated by the addition of methanol (2 ml) after 90s.

The polymer was purified by dissolving the gel in chloroform (6 ml) and adding the solution dropwise to methanol (100 ml) with swirling. This process was repeated three times to give the pure polymer (1.57 g) (78%).

This reaction was repeated on a smaller scale as a control experiment for each metathesis performed on other alkenes, using the same catalyst system.

2. Metathesis of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene

Metathesis of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (90 mg, 0.39 mmol) in chlorobenzene (1 ml) under similar conditions as in Section H.1, gave a polymer (64 mg,

71%). The ^{13}C -n.m.r. was poorly resolved and showed only the presence of CH groups. The molecular weight determination of the polymer was found to be $M_w = 40,000$ by gel permeation chromatography.

3. Attempted metathesis of 5,6:7,8-dibenzobicyclo[2.2.2]-octa-2,5,7-triene

The title compound (91 mg, 0.45 mmol) in chlorobenzene (1 ml) underwent attempted metathesis under similar conditions as the control. On addition of the catalyst the solution became very pale green, after 2 h the colour had disappeared but no increased viscosity of the solution occurred. After 24 h the chlorobenzene was evaporated and the resulting white solid was recrystallised from ethanol to give unreacted starting alkene (70 mg, 77%) as white crystals. Confirmation of this compound was given by its ^1H -n.m.r. spectrum.

4. Attempted metathesis of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

The title compound (80 mg, 0.45 mmol) in chlorobenzene (0.5 ml) underwent attempted metathesis under similar conditions as the control. Fifteen seconds after the addition of catalyst the solution became blue, after 24 h the colour remained and no increased viscosity in the solution was observed. The chlorobenzene was evaporated and the ^1H -n.m.r. spectrum of the remaining solid showed it to be the starting alkene.

5. Attempted metathesis of 3-thiabicyclo[4.3.0]non-7-ene
3,3-dioxide

Attempted metathesis of the title compound (108 mg, 0.63 mmol) in chlorobenzene (0.5 ml) under similar conditions as the control caused neither a colour change nor an increase in viscosity. After 20 h the solvent was evaporated and the ^1H -n.m.r. of the remaining white solid (95 mg) showed it to be the starting alkene.

6. Attempted metathesis of 4-thia-tricyclo[5.2.0^{1,7}0^{2,6}]-
non-8-ene-4,4-dioxide

The title compound (75 mg, 0.44 mmol) in chlorobenzene (0.5 ml) underwent an attempted metathesis under similar conditions as the control. The solution became blue 5s after the addition of the catalyst but no increase in viscosity was observed after 24 h. The chlorobenzene was evaporated and the resulting solid (65 mg, 87 %) was identified by its ^1H -n.m.r. spectrum as the starting alkene.

7. Attempted metathesis of 2,4-dioxo-3-oxabicyclo[3.2.0]-
hept-6-ene

2,4-Dioxo-3-oxabicyclo[3.2.0]hept-6-ene (124 mg, 1.00 mmol) in chlorobenzene (1 ml) underwent an attempted metathesis under similar conditions as the control. After the addition of the catalyst a green solution formed and after 23 h the colour was still apparent but no increase in viscosity was observed. The chlorobenzene was evaporated to give a pale green solid, whose ^1H -n.m.r. spectrum showed it to be the diacid of the starting material.

Further attempts to carry out a metathesis using molybdenum pentachloride instead of tungsten hexachloride in the catalyst system was unsuccessful on all the cyclic alkenes previously attempted including 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene.

8. Extrusion of anthracene from "Polycyclobutanthalracene"

A solution of the title compound, prepared in H.2, (52 mg) in chloroform (1 ml) was placed inside a test tube with a side arm and a film of "polycyclobutanthalracene" was deposited on the walls as the chloroform evaporated. A cold finger was placed inside the tube and the apparatus heated to 200°C under a vacuum of 1 mmHg. After 1 h a white solid (17 mg) was obtained on the cold finger and the previously clear film on the side of the tube became bright orange with speckles of black. The film was found not to conduct electricity, the white solid was shown to be anthracene (42% yield) by its ¹H-n.m.r. spectrum.

G. Preparation and FVP of 3-Thiabicyclo[3.2.0]hept-6-ene
3,3-Dioxide and Adducts

1. Preparation of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

(i) 3,5-Dioxo-4-oxa-9-thiatricyclo[5.3.0.0^{2,6}]decane
9,9-dioxide

This was prepared by a modification of the method of Shaikhrazieva *et al.*⁷⁹ A solution of butadiene sulphone (50 g, 424 mmol) and maleic anhydride (50 g, 510 mmol) in acetone (750 ml) was irradiated by a 400W medium pressure mercury lamp for 24 h, $\lambda=300\text{nm}$. The white crystals which had formed were filtered off and washed with ether to give 3,5-dioxo-4-oxa-9-thiatricyclo[5.3.0.0^{2,6}]decane 9,9-dioxide (45 g, 49%) as colourless crystals m.p. 292-293°C (lit.,⁷⁹ 292-293°C).

(ii) 3-Thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid
3,3-dioxide

3,5-Dioxo-4-oxa-9-thiatricyclo[5.3.0.0^{2,6}]decane 9,9-dioxide (45 g, 208 mmol) was dissolved completely in boiling water (150 ml). The solvent was evaporated to dryness and the solid residue was washed well with ether to give 3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 3,3-dioxide (45.0 g, 92%) as colourless crystals, m.p. 188-190°C (lit.,⁷⁹ 194-195°C).

(iii) 3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

A solution of 3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic acid 3,3-dioxide (4.92 g, 21.0 mmol) in dry pyridine (125 ml)

was oxygenated by bubbling oxygen through the solution for 15 min. Lead tetraacetate (vacuum dried, 13.8 g, 31.2 mmol) was added to the solution in one portion and the mixture heated to 67°C. After 10 min evolution of carbon dioxide was complete and the warm clear dark brown solution was poured into 5% nitric acid (1500 ml) and extracted with dichloromethane (4 x 250 ml). The organic extract was washed with aqueous sodium hydrogen carbonate and water, dried and the solvent was evaporated to give a brown oil. Kugelrohr distillation of the oil at 0.1 mmHg and 150-200°C gave a colourless semi-crystalline material. Recrystallisation from diisopropyl ether gave 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.685 g, 22%) as long colourless flakes, m.p. 72-74°C (lit.,⁸⁰ 71-75°C).

2. Reaction of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide with 1,3-dipoles and FVP of adducts

a. Attempted reaction with 1-piperidine^e 1-oxide

1-Piperidine^e 1-oxide (60 mg, 0.61 mmol) in toluene (0.5 ml) was added dropwise to a stirred solution of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (96 mg, 0.67 mmol) in toluene (5 ml). The reaction mixture was heated under reflux for 16 h during which time the colour of the reaction had darkened. The toluene was evaporated and the ¹H-n.m.r. spectrum of the residue showed that the alkene had not reacted.

3. Reaction of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide with 1,3-dienes and FVP of the cycloadducts

b. Attempted reaction with anthracene

A solution of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (200 mg, 1.39 mmol) and anthracene (340 mg, 1.9 mmol) in toluene was heated under reflux for 24 h. T.l.c. showed only the two starting materials were present. The toluene was evaporated and the ^1H -n.m.r. spectrum of the brown residue confirmed that only starting materials were present.

A repeat reaction using xylene instead of toluene as a solvent gave the same result.

c. Preparation of 1,9,10,11-tetraphenyl-5-thia-12-oxo-tetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodec-10-ene-5,5-dioxide

A solution of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (0.45 g, 3.1 mmol) and tetraphenylcyclopentadienone (1.20 g, 3.1 mmol) in benzene (25 ml) was heated under reflux for 64 h. Evaporation of the solvent gave deep red and white solids which were leached with ether, to remove unreacted cyclopentadienone, to give a white solid. Recrystallisation from benzene gave 1,9,10,11-tetraphenyl-5-thia-12-oxo-tetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodec-10-ene-5,5-dioxide (0.87 g, 55%) as colourless needles, m.p. 156-156.5°C (Found: C, 79.75; H, 5.55. $\text{C}_{35}\text{H}_{28}\text{O}_3\text{S}$ requires C, 79.55; H, 5.35%); ν_{max} 1780 (C=O), 1610 (C=C), 1315 (>SO_2) and 1140 cm^{-1} (>SO_2); δ_{H} (100MHz, CDCl_3) 2.66-2.85 (2H, m, C(3)H and C(7)H), 3.18-3.34 (4H, m, C(4)H₂ and C(6)H₂), 3.41-3.50 (2H, m, C(2)H and C(8)H) and 6.46-7.46 (20H, m, Ph); m/z 528 (M^+ , 0.8%), 500 (12) and 382 (100).

d. FVP of 1,9,10,11-tetraphenyl-5-thia-12-oxo-tetracyclo-
[7.2.1.0^{2,8}0^{3,7}]dodec-10-ene-5,5-dioxide

FVP of the title compound (0.569 g, 330°C, 4×10^{-3} mmHg, inlet 240°C) gave a white solid at the exit of the furnace, the i.r. spectrum of this compound showed a loss of the carbonyl peak (1780 cm^{-1}) which was present in the starting material. Recrystallisation from benzene gave 1,9,10,11-tetraphenyl-5-thia-tetracyclo[6.3.0^{1,8}0^{2,11}0^{3,7}]undec-9-ene-5,5-dioxide (0.350 g, 65%) as small colourless needles, m.p. 274-276°C (Found: C, 81.85; H, 5.6. $\text{C}_{34}\text{H}_{18}\text{O}_2\text{S}$ requires C, 81.55; H, 5.65%); ν_{max} 1600 (C=O), 1305 ($>\text{SO}_2$) and 1125 cm^{-1} ($>\text{SO}_2$); δ_{H} (200 MHz, CDCl_3) 2.94-3.08 (4H, m, C(4)H₂ and C(6)H₂), 3.30-3.43 (1H, m, CH) 3.50-3.63 (2H, m, C(3)H and C(7)H) 4.14 (1H, s, CH) and 6.90-7.18 (20H, m, Ph); δ_{C} (75MHz; CDCl_3) 38.28 (CH), 40.06 (CH), 52.71 (CH₂), 53.89 (CH), 56.81 (CH₂), 57.64 (quat. C), 59.57 (quat.C), 62.46 (CH), (126.15, 126.44, 126.63, 127.02, 127.47, 127.69, 127.69, 128.19, 128.42, 128.77, 128.85 and 129.77 (all aromatic CH)), 135.28, 136.02, 136.48, 137.47, 138.60 and 138.88 (aromatic and olefinic C); m/z 500 (M^+ , 40%) and 382 (100).

e. FVP of 1,9,10,11-tetraphenyl-5-thia-tetracyclo[6.3.0^{1,8}0^{2,11}0^{3,7}]undec-9-ene-5,5-dioxide

FVP of the title compound (65 mg, 675°C, 7×10^{-3} mmHg, inlet 200-230°C) gave a yellow solid (44 mg, 68%) at the liquid nitrogen level of the trap. The ^1H -n.m.r. spectrum of the crude material showed that only aromatic protons were present. Preparative t.l.c. of the material on alumina with *n*-hexane / ether (12:1) as eluant gave 1,2,3,4-tetraphenylbenzene (12 mg,

24%) at Rf 0.55. The ^1H -n.m.r. spectrum of this compound was confirmed by comparison with the standard ^1H -n.m.r. spectrum of 1,2,3,4-tetraphenylbenzene (lit.⁷¹).

f. Preparation of 1,9-diphenyl-5-thia-12-oxa-10,11-benzotetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodec-10-ene-5,5-dioxide

A solution of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (348 mg, 2.42 mmol) and 1,3-diphenylisobenzofuran (656 mg, 2.43 mmol) in benzene (25 ml) was heated under reflux for 15h

T.l.c. showed the disappearance of the starting alkene. Evaporation of the benzene afforded a yellow semi-solid which was dissolved in chloroform and added dropwise to hexane to give a white solid. The solid was recrystallised from ethanol-dichloromethane (4:1) which gave 1,9-diphenyl-5-thia-12-oxa-10,11-benzotetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodec-10-ene-5,5-dioxide (254 mg, 25%) as colourless needles m.p. 234-235°C (Found: C, 75.1; H, 5.2. $\text{C}_{26}\text{H}_{22}\text{O}_3\text{S}$ requires C, 75.35; H, 5.35%); ν_{max} 1600 (C=O), 1300 ($>\text{SO}_2$) and 1140 cm^{-1} ($>\text{SO}_2$); δ_{H} (100MHz; CDCl_3) 2.60-2.84 (2H, m, CH, CH), 2.94-3.20 (6H, m, C(4)H₂, C(6)H₂, CH, CH), 6.80-7.26 (4H, m, Ar) and 7.30-7.62 (10H, m, Ph); m/z 414 (M^+ , 0.3%), 396 (8), 332 (5), 270 (100), 241 (9), 165 (7), 105 (10) and 77 (12).

g. FVP of 1,9-diphenyl-5-thia-12-oxa-10,11-benzotetracyclo[7.2.1.0^{2,8}.0^{3,7}]dodec-10-ene-5,5-dioxide

FVP of the title compound (17 mg, 500°C, 6×10^{-3} mmHg, inlet 170-190°C) gave a yellow fluorescent liquid (9mg) at the exit of the furnace. The ^1H -n.m.r. spectrum of the liquid showed that 1,3-diphenylisobenzofuran was present but some divinyl

protons were also present in a small quantity. A repeat FVP at a slightly higher temperature (46 mg, 525°C, 7×10^{-3} mmHg, inlet 170-200°C) gave 1,3-diphenylisobenzofuran (25 mg, 83%), identified by ^1H -n.m.r. and by comparison with an authentic sample on t.l.c. on alumina with ether as eluant. The increase in temperature by 25°C showed a significant reduction in the size of the divinyl proton peaks in the ^1H -n.m.r. spectrum.

h. FVP of 9-phenyl-4-thia-8-oxotricyclo[5.3.0.^{1,7}₀^{2,6}]dec-9-ene-4,4-dioxide

The title compound was supplied by Dr. D.C. Billington of Strathclyde University. FVP of the title compound (18 mg, 550°C, 6×10^{-3} mmHg, inlet 230°C) gave a yellow product (10 mg) at the exit of the furnace. The ^1H -n.m.r. spectrum suggested that the product was a divinyl compound but the rest of the structure was difficult to interpret. Attempted purification of the compound by preparative t.l.c. on alumina with ether as eluant resulted in the decomposition or rearrangement of the product. The mass spectrum of the divinyl product m/z 429 (5%), 226 (59) and 210 (100) gave an unidentifiable parent peak but the peak at 210 was the peak expected for the divinyl compound. Analysis by g.l.c. proved to be unsuccessful, perhaps due to decomposition on the column to give several peaks.

4. Attempted preparation of thiepin 1,1-dioxide

a. Preparation of *E*-6,7-dibromo-3-thiabicyclo[3.2.0]heptane 3,3-dioxide

3-Thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (192 mg, 1.33 mmol) was dissolved in dichloromethane (1 ml) and added to carbon tetrachloride (25 ml). Bromine (500 mg, 3.13 mmol) was added dropwise with swirling of the solution and the mixture was heated under reflux for 19 h. On cooling white needles crystallised from the solution, these were filtered and washed with carbon tetrachloride. Recrystallisation from ethanol gave (*E*)-6,7-dibromo-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (348 mg, 86%) as colourless needles, m.p. 158-162°C (Found: C, 23.75; H, 2.6. $C_6H_8Br_2O_2S$ requires C, 23.7; H, 2.65%): ν_{\max} 1340 ($>SO_2$) and 1145 ($>SO_2$) cm^{-1} ; δ_H (80MHz; $CDCl_3$) 3.04-3.32 (2H, m, C(1)H and C(5)H), 3.32-3.80 (4H, m, C(2)H and C(4)H₂), and 4.52-4.96 (2H, m, C(6)H and C(7)H); m/z (M^+ , <1%), 223 (27), 159 (21), 119 (24) and 79 (100).

b. Preparation of 6-bromo-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

(*E*)-6,7-Dibromo-3-thiabicyclo[3.2.0]heptane 3,3-dioxide (566 mg, 1.86 mmol) in dimethoxyethane (30 ml) was added dropwise to a stirred solution of potassium tert-butoxide (443 mg, 3.72 mmol) in dimethoxyethane (40 ml) at room temperature under an atmosphere of nitrogen. After stirring for 24 h t.l.c. showed that no starting material was present. The solvent was evaporated and water added and the aqueous solution was extracted with dichloromethane (4 x 30 ml). The extract

was dried and evaporated to yield a white solid. Recrystallisation of the solid from ethanol gave 6-bromo-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (306 mg, 74%) as colourless needles, m.p. 102-104°C (Found: C, 32.4; H, 3.26. $C_6H_7BrO_2S$ requires C, 32.25; H, 3.15%); ν_{\max} 1300 (SO₂) and 1130 cm⁻¹ (SO₂); δ_H (100MHz; CDCl₃) 2.90-3.30 (4H, m, C(2)H₂ and C(4)H₂), 3.62-4.00 (2H, m, C(1)H and C(5)H) and 6.30 (1H, s, C(7)H); m/z 222 (M⁺, 55%), 158 (13), 95 (13) and 77 (100).

c. Attempted dehydrobromination of 6-bromo-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

6-Bromo-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide was added to several solutions of bases for example, sodium methoxide (60°C), potassium tert-butoxide (70°C, 85°C) lithium di-isopropylamide (20°C) with reaction times of 24 to 64 h but in all cases only the starting bromo-alkene was recovered.

d. Photolysis of 6-bromo-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

A solution of 6-bromo-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (60 mg, 0.27 mmol) in d-chloroform (2 ml) was placed in a quartz n.m.r. tube and irradiated by a 125W medium pressure mercury lamp for 75 min. The ¹H-n.m.r. spectrum showed that only starting material was present. The solution was irradiated for a further 65 min by a 400W lamp. The ¹H-n.m.r. spectrum of the partially charred solution showed that no rearrangement had occurred.

H. Synthesis of Bicyclo[2.2.0]hexa-2,5-diene (Dewar Benzene).

1. Preparation of (Z)-1,2-di(hydroxymethyl)cyclobut-3-ene

2,4-Dioxo-3-oxabicyclo[3.2.0]hept-6-ene (10.38 g, 84 mmol) was dissolved in dry tetrahydrofuran (250 ml) and added dropwise to a stirred suspension of lithium aluminium hydride (5.3 g, 141 mmol) in dry tetrahydrofuran (50 ml) under nitrogen and the mixture was heated under reflux for 2 h. On cooling the excess lithium aluminium hydride was destroyed by the addition of 90% aqueous tetrahydrofuran (35 ml) followed by 15% sodium hydroxide solution (5 ml) and finally water (15 ml). The inorganic solids were filtered off and washed with dichloromethane (250 ml). The combined filtrates which were dried and evaporated gave (Z)-1,2-di(hydroxymethyl)cyclobut-3-ene (8.79 g, 92%) as a pale yellow oil. The ^1H -n.m.r. spectrum δ_{H} (60MHz; CDCl_3) 2.96-3.90 (6H, m, CH_2 and CH), 5.61 (2H, s, OH), 6.03 (2H, s, C(3)H and C(4)H) confirmed that the diol was pure by comparison with the ^1H -n.m.r. spectrum of the authentic sample.⁸¹

2. Preparation of (Z)-1,2-di(p-toluene sulphonoxymethyl)-cyclobut-3-ene

1,2-Di(hydroxymethyl)cyclobut-3-ene (8.79 g, 77 mmol) was dissolved in pyridine (26 ml) and the solution was added to a suspension of p-toluene sulphonyl chloride (45.9 g, 241 mmol) in pyridine at 0°C and stirred at this temperature

for 3 h. The solution was poured into 10% sulphuric acid (600 ml) and extracted with dichloromethane (5 x 200 ml). The extract was washed with water, dried and evaporated to dryness to afford a yellow oil, which crystallised on standing. Recrystallisation of the solid from ethanol gave (Z)-1,2-di(*p*-toluene sulphonoxymethyl)cyclobut-3-ene (30.8 g, 95%) as colourless crystals, m.p. 66-68°C. The ^1H -n.m.r. δ_{H} (100MHz; CDCl_3) 2.42 (6H, s, CH_3), 3.28 (2H, t, J 6Hz, C(1)H and C(2)H), 4.06 (4H, d, J 7Hz, CH_2), 5.95 (2H, s, C(3)H and C(4)H), 7.32 (4H, d, J 8Hz, Ar) and 7.72 (4H, d, J 8Hz, Ar) gave the expected spectrum and was identical to the authentic sample.⁸¹

3. Preparation of 3-thiabicyclo[3.2.0]hept-6-ene

A solution of (Z)-1,2-di(*p*-toluene sulphonoxymethyl)-cyclobut-3-ene (30.0 g, 71 mmol) and sodium sulphide nonahydrate (58 g, 241 mmol) in an ethanol/water (1:1) mixture (500 ml) was heated under reflux for 16 h. The ethanol was removed under reduced pressure at room temperature and the aqueous solution was extracted with dichloromethane (4 x 200 ml). Drying and evaporation of the extract gave 3-thiabicyclo[3.2.0]hept-6-ene (4.91 g, 62%) as a pale yellow oil with a foul smell. The ^1H -n.m.r. δ_{H} (60MHz; CDCl_3) 2.5-2.7 (4H, m, C(2)H₂ and C(4)H₂), 3.4-3.7 (2H, m, C(1)H and C(5)H) and 5.9 (2H, s, C(6)H and C(7)H) was comparable to the authentic sample.⁸¹

4. Preparation of 2-chloro-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

N-Chlorosuccinimide (5.85 g, 44 mmol) was added to a

stirred solution of (Z)-3-thiabicyclo[3.2.0]hept-6-ene (4.91 g, 44 mmol) in dry dichloromethane (50 ml) at 0°C and the mixture was stirred for 16 h. The milky-yellow solution was filtered, to remove the succinimide, to give a yellow filtrate.

m-Chloroperoxybenzoic acid (85%, 17.80 g, 88 mmol) was added to the stirred yellow filtrate, 2-chloro-3-thiabicyclo[3.2.0]hept-6-ene, (6.47 g, 44 mmol, assuming 100% chlorination in the foregoing step) at a temperature of 0°C and the mixture was stirred for 64 h, allowing the temperature to rise to 20°C. T.l.c. showed that no starting material remained and the solution was washed with aqueous sodium carbonate (4 x 25 ml), dried and the solvent was evaporated to yield a white solid. Recrystallisation of the solid from diisopropylether gave 2-chloro-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (1.62 g, 21%) as colourless crystals, m.p. 78-79°C (Found: C, 40.55; H, 4.05. $C_6H_7ClO_2S$ requires C, 40.35; H, 3.95%); ν_{\max} 1320 ($>SO_2$) and 1120 cm^{-1} ($>SO_2$); δ_H (100MHz, $CDCl_3$) 3.20-3.31 (2H, m, C(4)H₂), 3.69-3.78 (2H, m, C(1)H and C(5)H) 4.67 (1H, s, C(2)H and 6.21 (2H, s, C(6)H and C(7)H); *m/z* 178 (M^+ , 3%), 143 (3), 115 (2), 101 (3), 79 (100) and 77 (41).

5. Reaction of 2-chloro-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide with potassium *t*-butoxide

Potassium *t*-butoxide (1.01 g, 8.4 mmol) was added in one portion to a solution of 2-chloro-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (177 mg, 0.99 mmol) in tetrahydrofuran (12 ml) at -78°C. A yellow solution formed immediately and after 5 min a slight effervescence was observed in the solution. The

solution was stirred for 17 h during which time the solution was warmed slowly to 18°C to give a red solution. Water (50 ml) was added to the reaction mixture and the aqueous solution was extracted with pentane (3 x 50 ml). The extract was washed with water (3 x 50 ml), dried and the solvent was evaporated at 25°C. The ¹H-n.m.r. spectrum showed the colourless liquid to contain mainly pentane and tetrahydrofuran. Analysis by g.l.c. on 5% Carbowax at 45°C confirmed, by comparison with authentic samples, that tetrahydrofuran and pentane were present and that no benzene was present.

The reaction was repeated but following the pentane extraction, bromine (500 mg, 3.1 mmol) in pentane (5 ml) was added to the pentane extract and the solution was stirred for 18 h. The pentane was evaporated to give a dark brown free flowing liquid (300 mg). Chromatography on alumina with ether as eluant gave a free flowing brown oil. The ¹H-n.m.r. spectrum showed that no starting material was present and that none of the products were identifiable. The mass spectrum of the compound gave a pattern of peaks at 398 which was characteristic of a tetrabromide and indicated that C₆H₆Br₄ was present. (Found M⁺ 397.715016. C₆H₆Br₂⁷⁹Br₂⁸¹ requires 397.716568).

6. Preparation of 2-bromo-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

This compound was prepared by a modification of the method by K.B. Becker.⁸²

A solution of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (405 mg, 2.81 mmol) in ether (5 ml) and benzene (5 ml) was added dropwise to a solution of ethylmagnesium bromide (372 mg,

2.80 mmol) in ether (10 ml) at 0°C under an atmosphere of nitrogen. The solution was heated under reflux for 3 min and cooled to 0°C. A solution of bromine (375 mg, 2.34 mmol) in benzene (4 ml) was added dropwise to the cooled solution. The resulting solution of a yellow suspension was stirred at 20°C for 2 h. Water (10 ml) was added to the solution and the organic phase was washed with aqueous ammonium chloride (3 x 25 ml) and water (2 x 25 ml), dried and evaporated to dryness to give a brown oil (0.482 g). Recrystallisation from diisopropyl ether afforded 2-bromo-3-thiabicyclo[3.2.0]-hept-6-ene 3,3-dioxide (305 mg, 48%) as off-white crystals m.p. 74-76°C; δ_{H} (80MHz; CDCl_3) 3.18-3.90 (4H, m, C(4)H₂, C(1)H and C(5)H), 4.68-4.90 (1H, m, C(2)H) and 6.15-6.26 (2H, m, C(6)H and C(7)H); m/z 222 (M^+ , 69%) and 158 (100). (Found M^+ 221.939389. $\text{C}_6\text{H}_7^{79}\text{BrO}_2\text{S}$ requires 221.935064).

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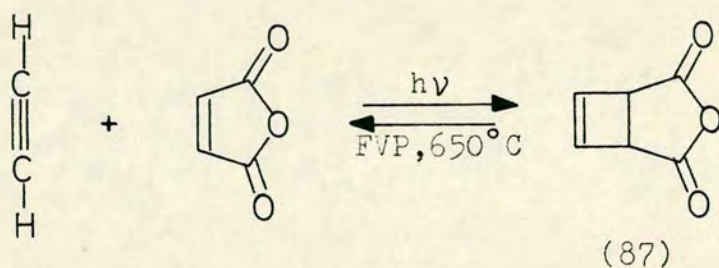
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A. Preparation and pyrolysis of some derivatives of
2,4-dioxo-3-oxabicyclo[3.2.0]hept-6-ene

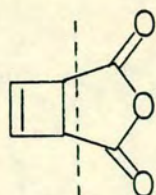
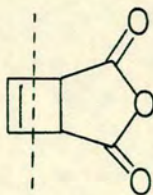
1. General background

Numerous examples of the synthesis and reactions of cyclobutenes fused to heterocyclic ring systems have been reported in the literature.⁸³ 2,4-Dioxo-3-oxabicyclo[3.2.0]hept-6-ene (cyclobutene anhydride) (87) is a member of this group and has been prepared in good yield⁶³ from the photochemical reaction of maleic anhydride with acetylene, both of which are comparatively cheap starting materials. The ease of its accessibility, cheapness and potential reactivity

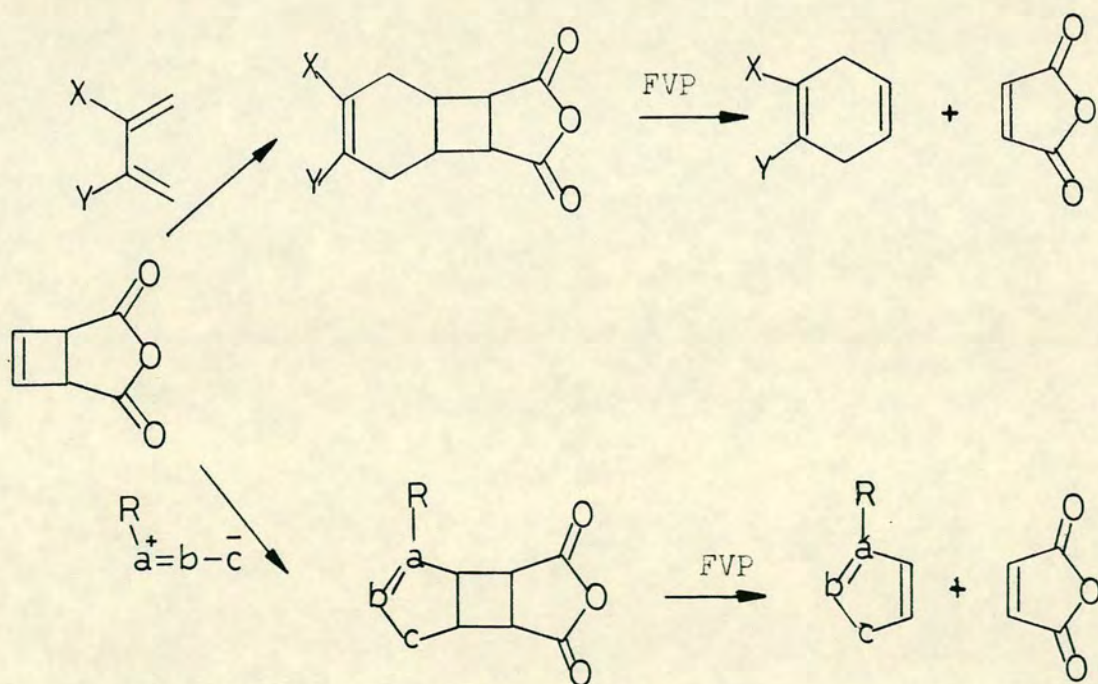


suggested the anhydride (87) might provide a way of producing a wide range of novel and useful hetero- and carbocycles. This potential derives from the prospect of (87) serving as a cyclobutadiene synthon (see fig 3 a) by loss of carbon monoxide and carbon dioxide, or as an acetylene equivalent (see fig 3 b) by loss of maleic anhydride.

At an early stage it was discovered that flash vacuum pyrolysis (FVP) of (87)⁸⁴ at 650°C gave mainly maleic anhydride, and it was this ability to lose acetylene readily under

fig 3afig 3b

pyrolytic conditions that led to an investigation of its use as an acetylene synthon. This strategy depended on the ability of (87) to react as a dienophile or 1,3 dipolarophile to form an adduct which could subsequently undergo pyrolysis to selectively cleave maleic anhydride from the molecule and give rise to a cyclo-adduct with a carbon carbon double bond, as shown in Scheme 25.

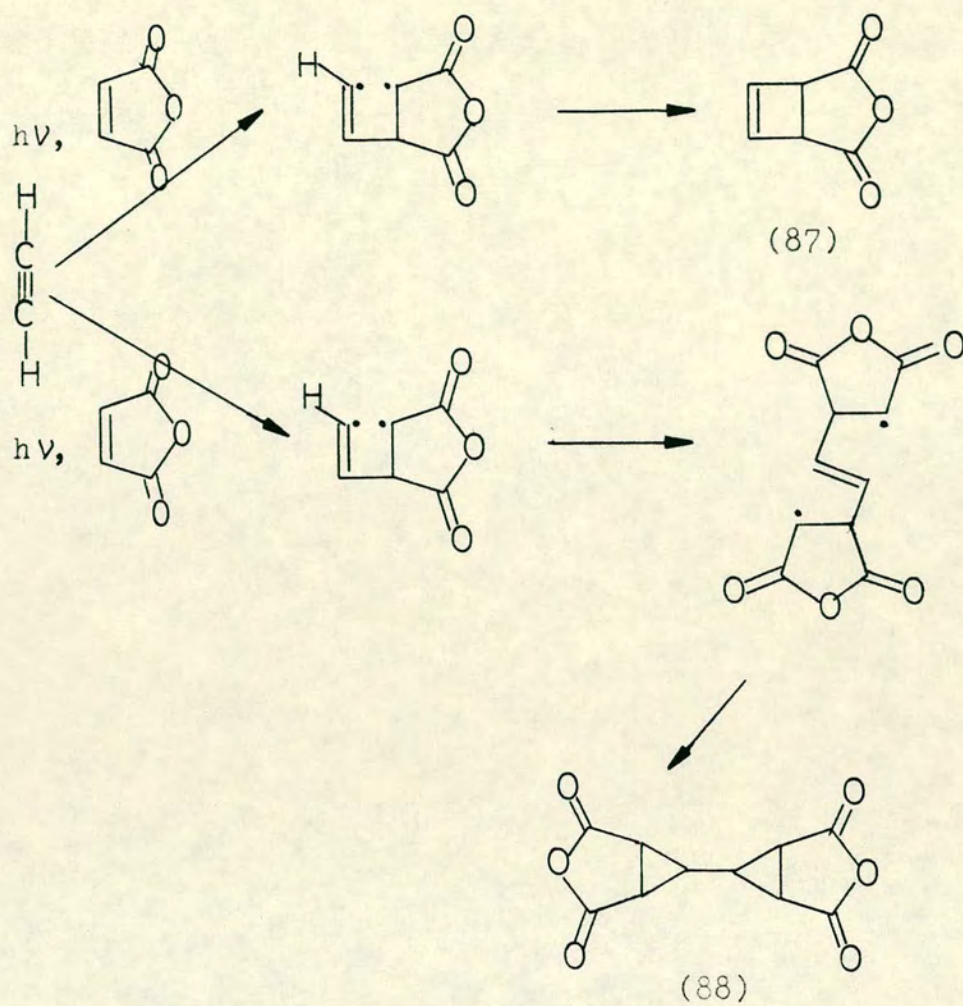
Scheme 25

In preliminary studies in this laboratory Tinley had investigated the reactivity of the strained cyclobutene double bond with reagents known to add to such a function, and subsequently examined the thermal and chemical characteristics

of the resulting cyclobutanes. In the course of the present study, improvements to the synthesis of the anhydride (87) were made and the limitations to its synthetic usefulness were examined.

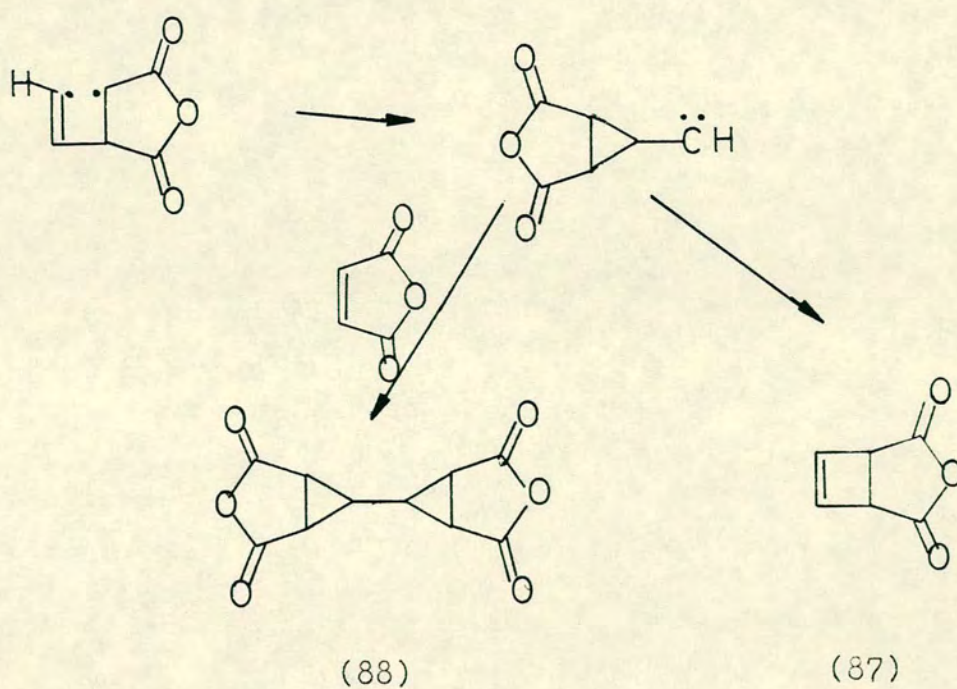
It was discovered that during the photochemical ($2\pi+2\pi$) addition of the acetylene to maleic anhydride it was critical to keep the reaction temperature at -78°C in order to prevent the ready formation of the cyclopropane dimer (88).⁶⁴ Some of this dimer is invariably formed during the reaction at -78°C , but usually accounts for only 20% of the reactants. Two mechanisms, both of which are given in Schemes 26 and 27, have been proposed^{64,65} to explain the formation of both (87) and its accompanying cyclopropane by product (88).

The use of a photosensitiser in the reaction was necessary, but no difference was observed between acetophenone and benzophenone in terms of the yield of product obtained. Benzophenone was preferred, rather than acetophenone, due to the similarity of the boiling points of the anhydride (87) and acetophenone in the distillation during the work up. The distilled cyclobutene anhydride was recrystallised from diisopropyl ether to give a stable crystalline solid in 49% yield.



Scheme 26

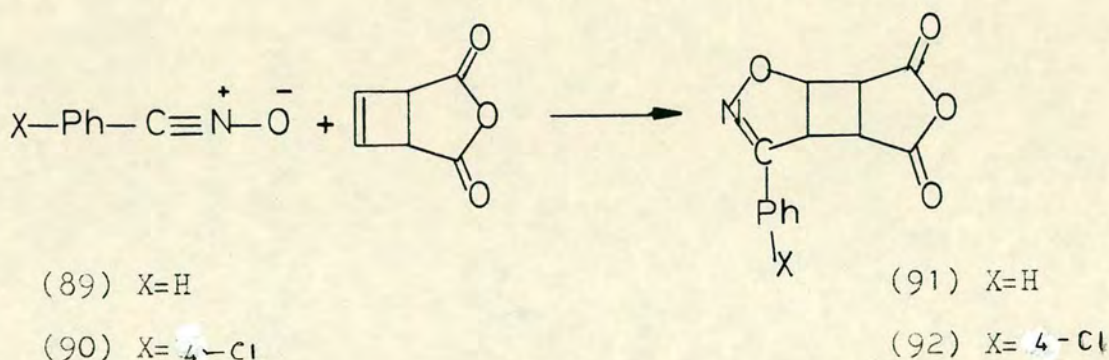
OR



Scheme 27

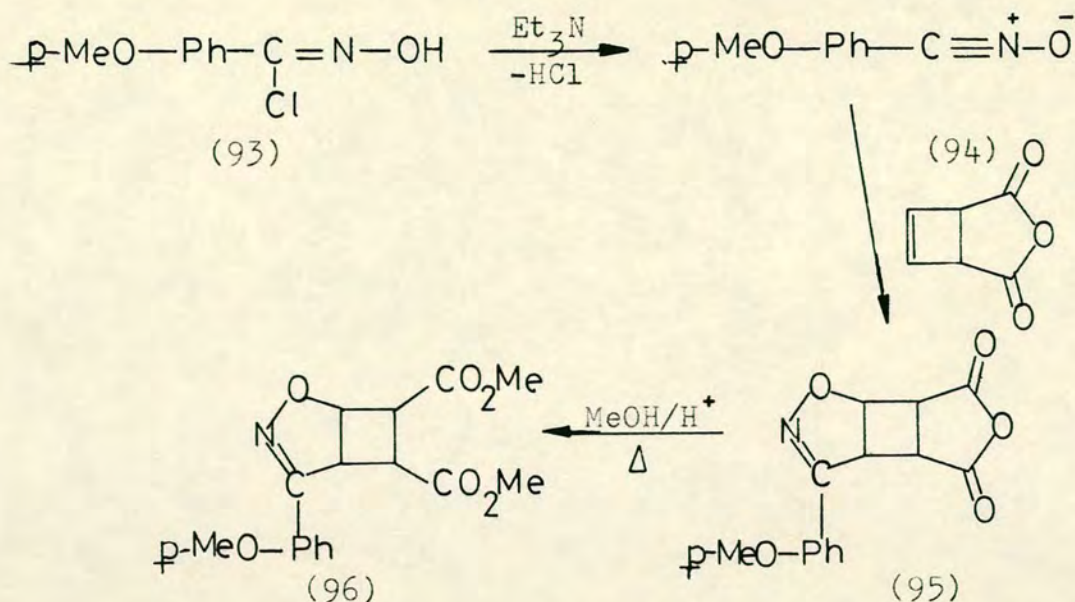
2. Addition of 1,3 dipoles to 2,4-dioxo-3-oxabicyclo-[3.2.0]hept-6-ene and FVP of its adducts

In previous work Tinley⁸⁶ had successfully reacted two nitrile oxides, namely benzonitrile oxide (89) and *p*-chlorophenyl nitrile oxide (90), with cyclobutene anhydride (87) to give adducts (91) and (92) yields of 58% and 85% respectively. As part of the present studies, an attempt was made to extend this work by examining its reaction with various other 1,3 dipoles.



Scheme 28

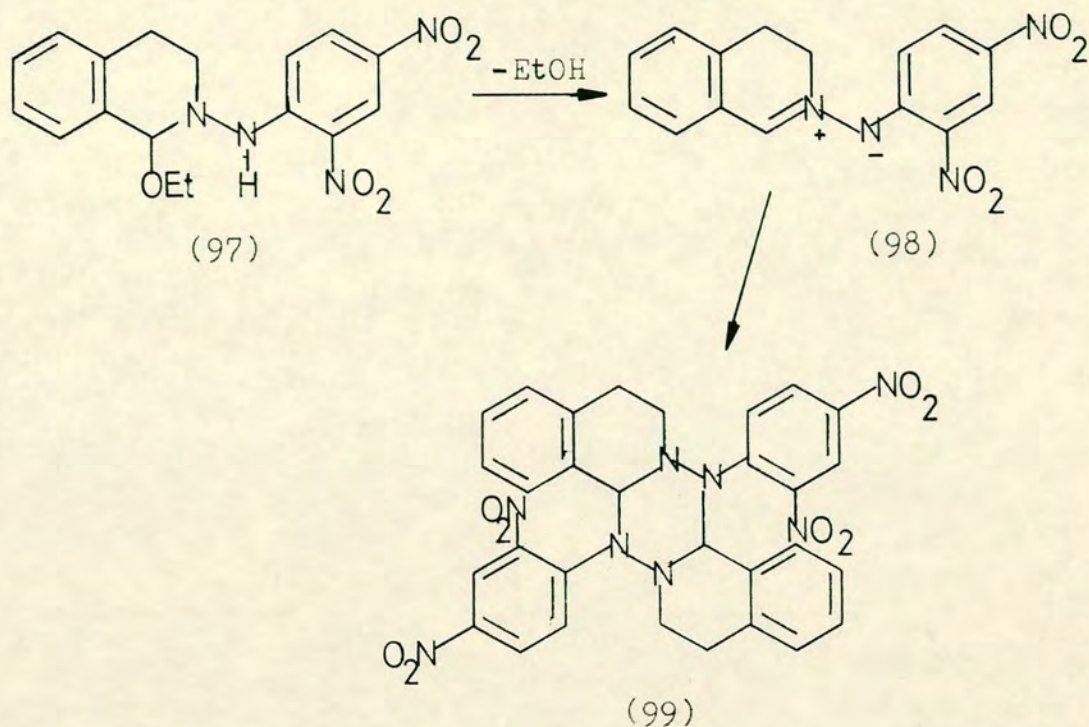
Two substituted phenyl nitrile oxides, *p*-methoxy- and *p*-nitrophenyl nitrile oxides, were generated in the presence of the cyclobutene anhydride (87). The *p*-methoxyphenyl nitrile oxide (94) was formed from the corresponding hydroximoyl chloride (93) by elimination of HCl with triethylamine at room temperature. The derived adduct (95), formed by reaction of the anhydride with the nitrile oxide (94) at 20°C, was found to have undergone partial hydrolysis during work up, to form the corresponding diacid, as evidenced by ¹H-n.m.r. and i.r. spectroscopy. As a result the mixture of anhydride and



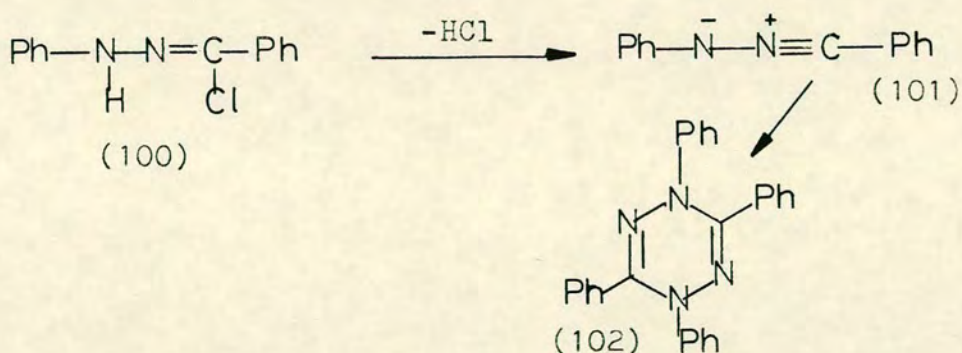
Scheme 29

diacid was esterified by acid catalysis in methanol to give the dimethyl ester (96), albeit in a relatively low yield of 30%. The corresponding reaction of *p*-nitrophenylnitrile oxide with cyclobutene anhydride did not occur under similar conditions, nor even by heating the reactants with and without base under reflux in toluene. In the reaction of the *p*-nitrohydroximoyl chloride with base, the nitrile oxide was shown to have been generated as evidenced by the presence of triethylamine hydrochloride, but it failed to add across the double bond.

Thus, several other 1,3 dipoles failed to react, including the azomethine imine (98), whose mode of formation relied upon the thermal extrusion of ethanol from 1-ethoxyl-2-(2,4-dinitroanilino)-1,2,3,4-tetrahydroisoquinoline (97).⁶⁶ Apparently, it preferred to form the dimer (99) rather than form an adduct with the cyclobutene anhydride (87). The dimer was obtained in the form of yellow brown crystals,⁶⁸ and was identified by $^1\text{H-n.m.r.}$ spectroscopy.

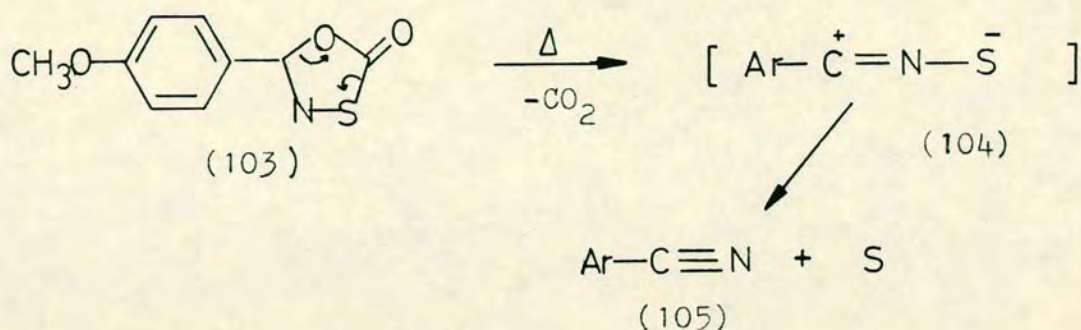


Diphenylnitrileimine (101), generated either by thermal or homogenous base-induced elimination of HCl from diphenylhydrazidoyl chloride (100), also failed to react with cyclobutene anhydride (87), but did form a dimer with itself (102).



In another experiment, *p*-anisonitrile sulphide (104) was generated in the presence of cyclobutene anhydride (87) by the thermolysis of oxathiazalone (103) in boiling xylene; even by using a large excess of (103) and prolonged reaction times, none of the desired cycloadduct was formed. It is worth noting that cycloaddition reactions of nitrile sulphides are complicated

by a facile competitive degradation to nitriles (105) and sulphur,⁹⁰ and the lack of reactivity in this instance is not really surprising in view of the foregoing failures.



The poor reactivity of (87) was further confirmed by its surprising failure to react with ethyl azidoformate,^{87,88} even under photolytic conditions.

The foregoing results of the reaction of cyclobutene anhydride (87) with various 1,3-dipolar reagents are summarised in Table 1.

In Diels-Alder reactions, endo-adducts are formed rather than the alternative exo-adducts. This is due to secondary orbital interactions within the cycloadduct. It is possible to show the formation of an endo-adduct by the presence of a cis-coupling constant in the ¹H n.m.r. spectrum. For example, in the formation of dimethyl 4-(p-methoxyphenyl)-2-oxa-3-azabicyclo[3.2.0]hept-3-ene-6,7-dicarboxylate (p. 48) the ¹H n.m.r. data gave a coupling constant of 8 Hz on the C(1)H and C(5)H which was indicative of cis-coupling with the protons on C(7) and C(6) respectively.

Table 1. Reaction between cyclobutene anhydride and
1,3 dipolar reagents

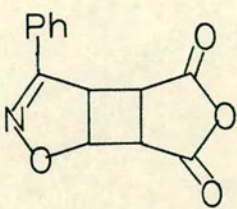
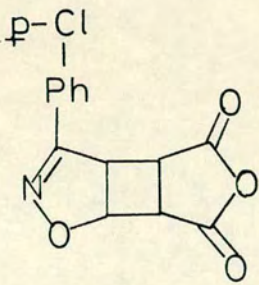
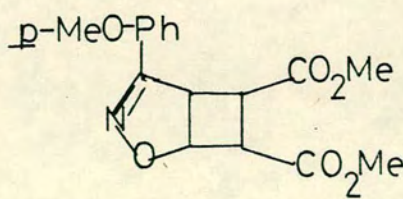
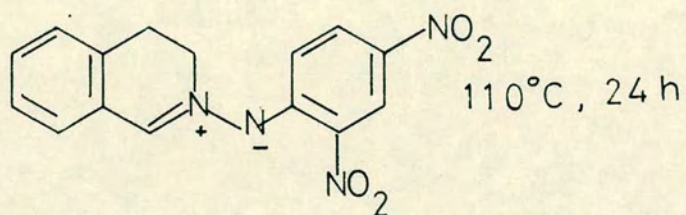
<u>Reagent</u>	<u>Conditions</u>	<u>Adduct</u>	<u>Yield</u>
$X\text{-Ph-}\overset{+}{\text{C}}=\text{N-O}^-$			
X=H	20°C, 3h		58%
X=Cl	20°C, 3h		85%
X=NO ₂	110°C, 6h	—	NR
X=MeO	20°C, 3h		30%
$\begin{array}{c} \text{Cl} \quad \text{H} \\ \quad \\ \text{Ph-C}=\text{N-N-Ph} \end{array}$	20°C, 120h 140°C, 72h	—	NR

Table 1 (continued)

<u>Reagent</u>	<u>Conditions</u>	<u>Adduct</u>	<u>Yield</u>
$\text{EtO}_2\text{C}-\text{N}_3$	$h\nu$, 48h	—	NR

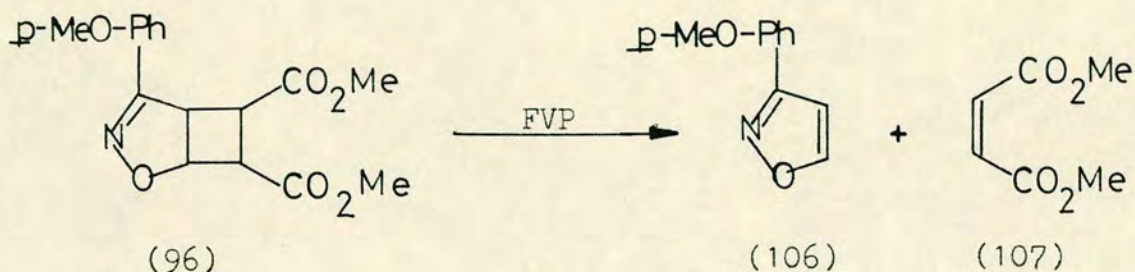


—

NR

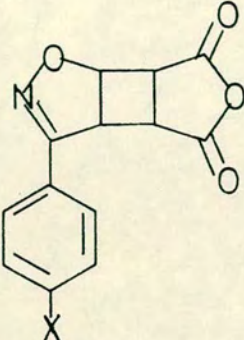
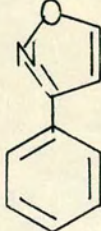
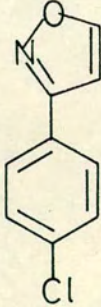

NR= No Reaction

The F.V.P. of the dimethyl ester adduct (96) at 600°C resulted in the expected cleavage of dimethyl maleate (107) from the molecule. The 3(p-methoxyphenyl)isoxazole (106) was obtained in 64% yield after preparative t.l.c. of the crude pyrolysis product. The ^1H -n.m.r. spectrum of the isoxazole (106) compared favourably with that of similar isoxazoles synthesised by Tinley⁸⁶ (see Table 2 for conditions and yields).



Although perturbation treatment performs less well with the comparison of widely different dipoles and their reaction with a single alkene, it is possible to explain the pattern of reactivity of (87) with 1,3-dipoles by using molecular orbital theory. In the frontier orbital approach of Houk,⁸⁹ for a dipole LUMO controlled process, as might be expected here, the key value is the energy gap between the LUMO of the 1,3 dipole and the HOMO of the dipolarophile. If this gap is small then the transition state will be significantly stabilised and the reaction is likely to take place. Thus for any given dipolarophile, those dipoles with the lowest LUMO energy will react most readily in a LUMO controlled process. Houk⁸⁹ gives the LUMO energies for many of the 1,3 dipoles used in this

Table 2. FVP results of 1,3 dipolar cycloadducts with
cyclobutene anhydride

<u>Substrate</u>	<u>Furnace</u> <u>Temperature</u>	<u>Product</u>	<u>Yield</u>
 <p>X=H</p>	600°C		71%
X=Cl	510°C		19%
X=MeO	600°C		64%

study and the values are in good agreement with the observed reactivity.

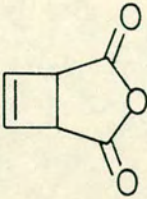
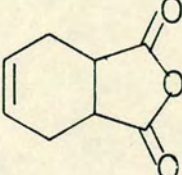
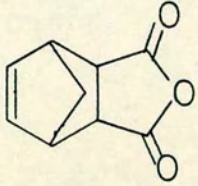

Benzonitrile oxide, for example, with a LUMO of -1.0eV ,⁸⁹ reacts readily while diphenyl nitrile imine (-0.5eV)⁸⁹ does not. Since the value for benzonitrile sulphide is 0.0eV ,⁹⁰ a substituent of a *p*-MeO group as in (103) would probably raise this value slightly. This probably accounts for the lack of reactivity in this instance. However the azomethine imine (98) which has a LUMO value of -1.4eV ,⁸⁹ might have been expected to react with (87) but it does not. The reason for the failure of this reaction is not certain since azomethine imines, with low LUMO and high HOMO energy levels are known to react readily with all types of alkenes.

3. Preparation and FVP of Diels-Alder adducts of 2,4-dioxo-3-oxa-bicyclo[3.2.0]hept-6-ene

The failure of the cyclobutene anhydride (87) to react with many of the reagents in the previous section may be attributed to the fact that the double bond is relatively electron deficient. This is reflected in the unusually high ionisation energy (π^{Ip}) of (87) which was found to be 10.49eV . From a comparison of this value with those of comparable alkenes,⁹¹⁻⁹³ given in Table 3, it is evident that there is a net mixing of the carbonyl molecular orbital with the π molecular orbital which results in a lowering of the energy level of the latter orbital.

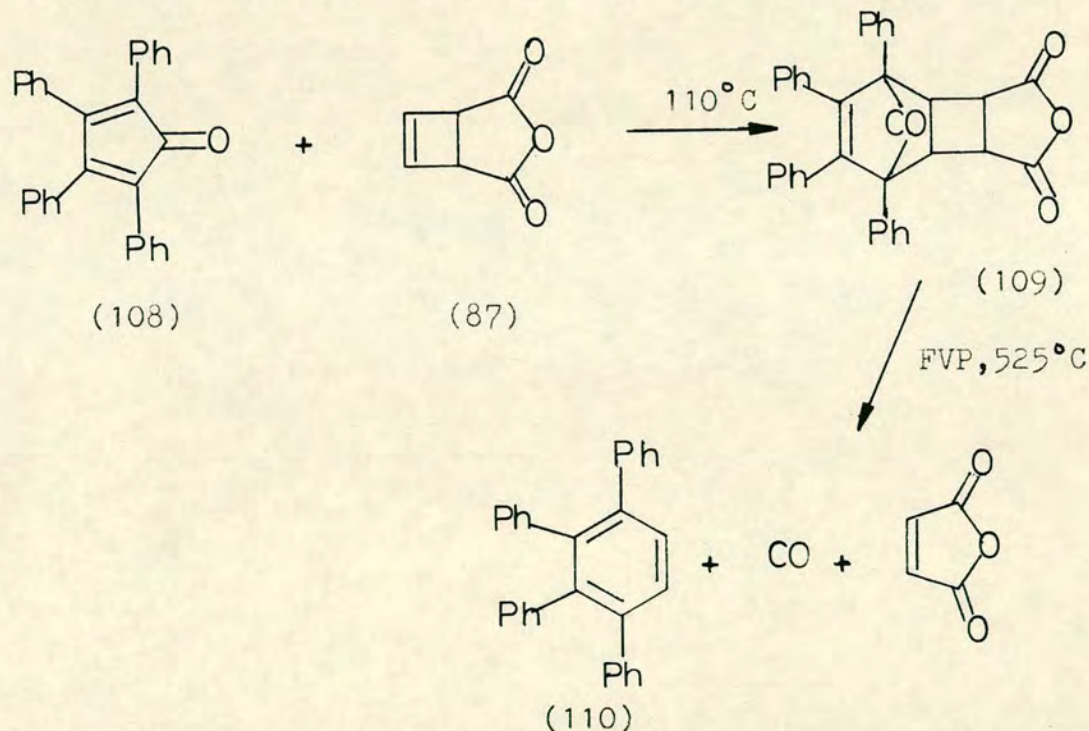
However an electron deficient alkene can be particularly reactive with electron rich dienes in the Diels-Alder reaction and an attempt was made to carry out some of these reactions

Table 3. Vertical ionisation potentials (eV) for
cyclobutene anhydride (87) and comparison
olefins

<u>Olefin</u>		<u>π Ip</u>
		10.49 ⁹¹
		10.02 ⁹¹
	exo endo	9.61 ⁹² 9.85
		8.97 ⁹³

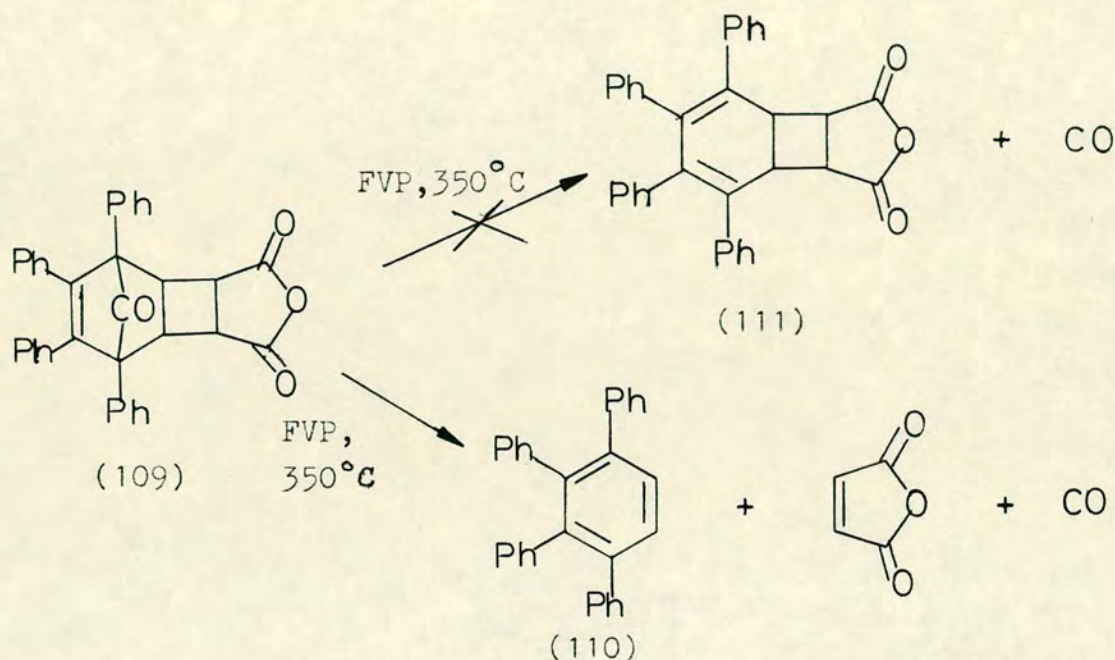
with cyclobutene anhydride.

The reaction between 1,2,3,4-tetraphenylcyclopentadienone (108) and cyclobutene anhydride (87) was found to proceed readily in benzene at 80°C to give a 42% yield of the adduct (109) as a colourless, crystalline solid which showed a strong absorbance at 1780 cm^{-1} in its infra-red spectrum. This adduct (109) was found to decompose at its melting point. When subjected to flash vacuum pyrolysis at 525°C, the adduct (109) fragmented to afford maleic anhydride as a colourless solid at the N_2 level of the FVP trap, and a yellow liquid in a yield of 45%, at the exit of the furnace. The latter product

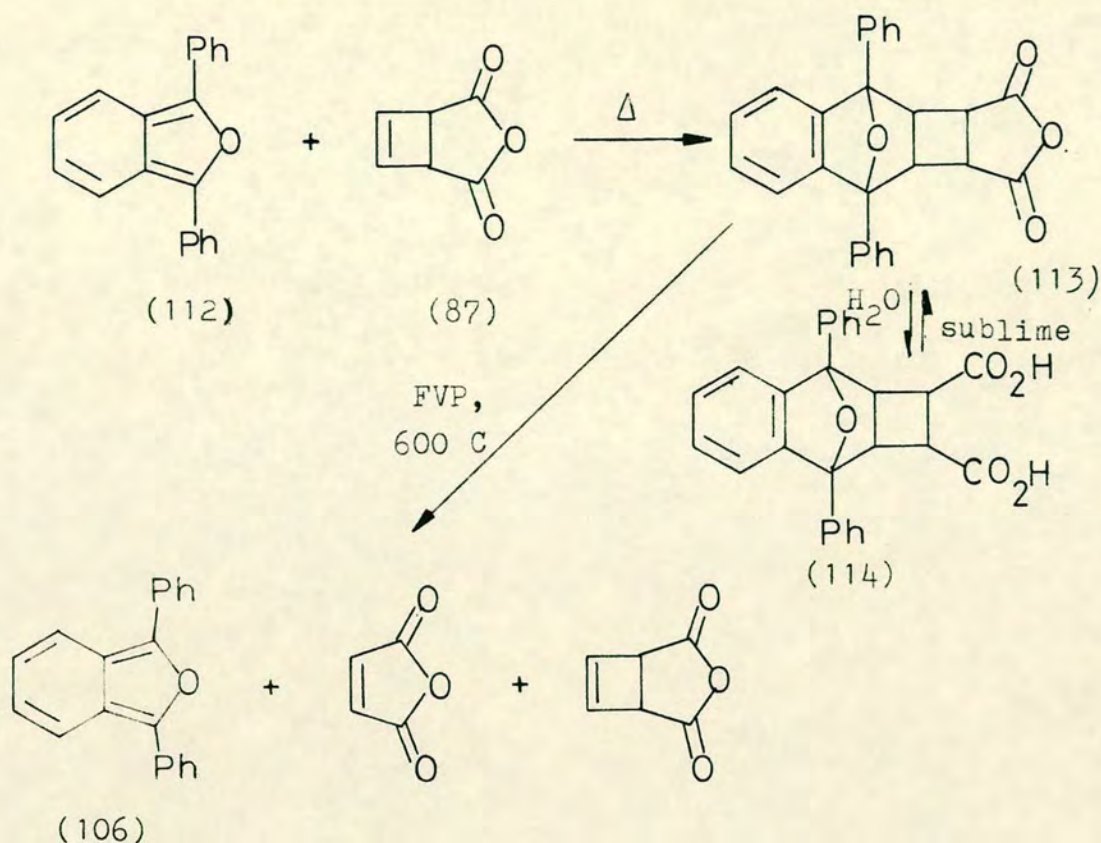


was identified conclusively as 1,2,3,4-tetraphenylbenzene (110) by comparison with the spectral and glc characteristics of an authentic sample. Clearly, in this instance, the ease of pyrolysis was due to the formation of an aromatic ring which obviously provided a large driving force for the pyrolytic cleavage. In an attempt to extrude only carbon

monoxide, (see also section E4), the adduct (109) was pyrolysed at 350°C but under these conditions 1,2,3,4-tetraphenylbenzene (110) was formed, albeit in a yield of only 25%, with no indication of the formation of the desired product (111).



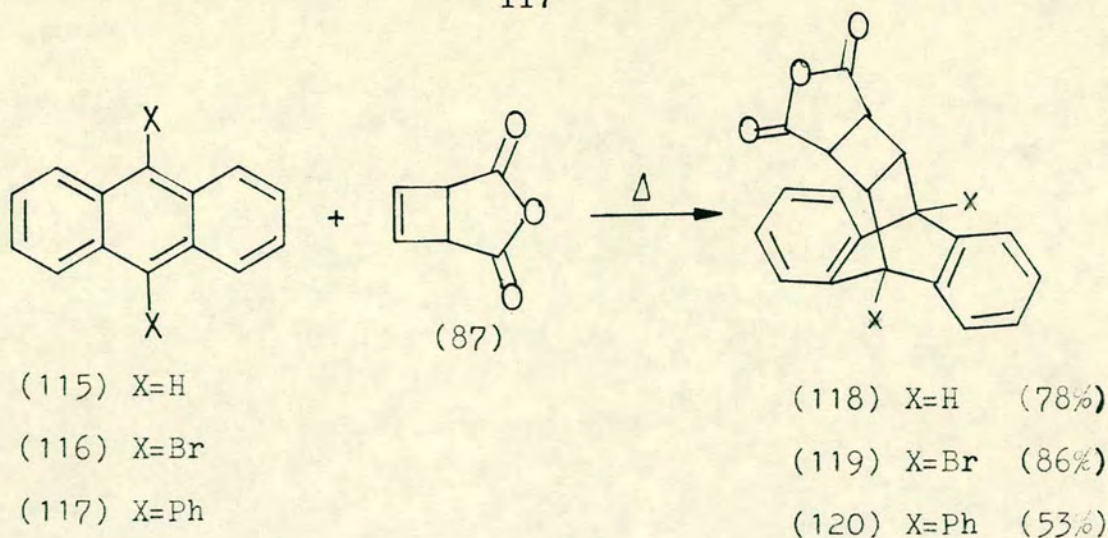
In the related reaction of (87) with 1,3-diphenylisobenzofuran (112) a partially hydrolysed product (114) was obtained which sublimed to give the pure adduct (113) in a 68% yield. Under F.V.P. conditions at 600°C (113) decomposed to give predominantly maleic anhydride (55%) and 1,3 diphenylisobenzofuran (98%). Analysis of the reaction by ^1H -n.m.r. spectroscopy showed that a small amount of cyclobutene anhydride (<5%) was also present. In this case it is likely that (113) fragmented by a retro-Diels-Alder reaction to give 1,3 diphenylisobenzofuran and cyclobutene anhydride (87), which was further degraded to give maleic anhydride by loss of acetylene.



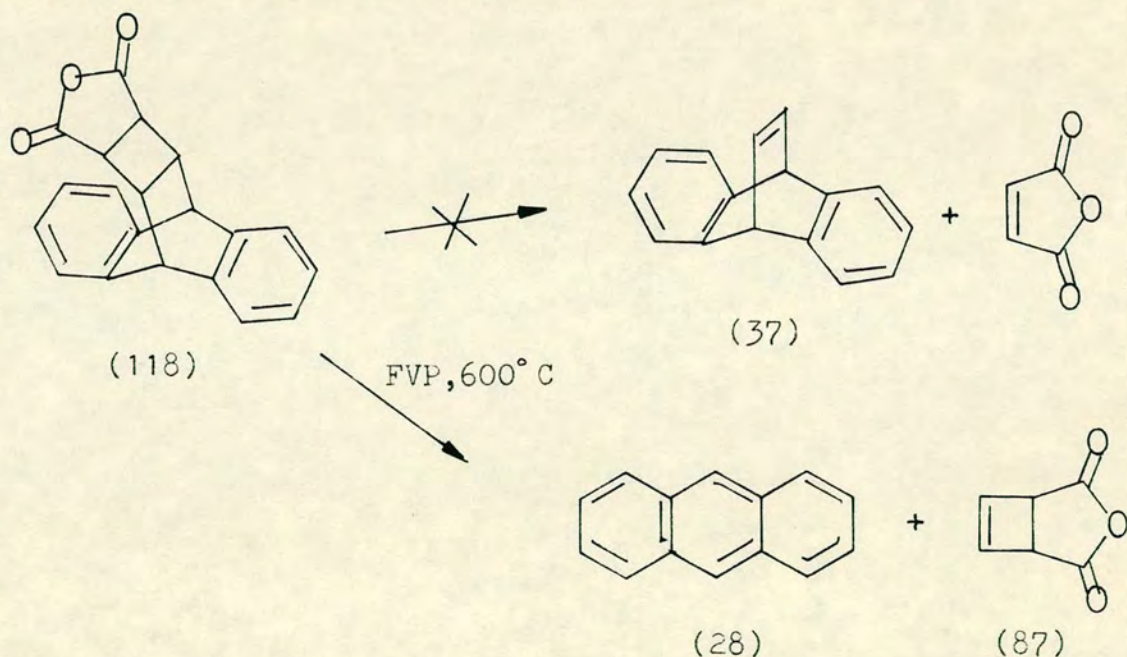
Scheme 30

Cyclobutene anhydride (87) reacted readily with anthracene (115), 9,10-dibromoanthracene (116) and 9,10-diphenylanthracene (117) in boiling toluene, (no reactions occurred in boiling benzene). The adducts were obtained in moderate to good yields as stable, crystalline compounds, the structures of which were confirmed by elemental analysis and their complementary spectral data.

It was hoped that under F.V.P. conditions, the adduct (118) would fragment to form dibenzobarrelene (37) and maleic anhydride. However at 600°C, the adduct preferred to undergo a virtually quantitative retro-Diels-Alder reaction to form anthracene (28) and cyclobutene anhydride (87). As in the case of adduct (113), the driving force of this reaction



was obviously the formation of an aromatic molecule.

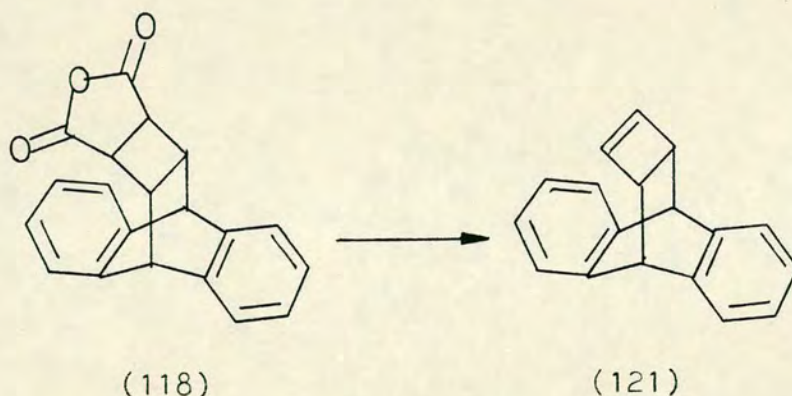


The substituted adducts (119) and (120) were not pyrolysed but used synthetically at a later stage, (see section B.3.).

In conclusion although cyclobutene anhydride serves as an acetylene synthon in certain reactions, it does not in others. In particular, cyclobutene anhydride is a useful

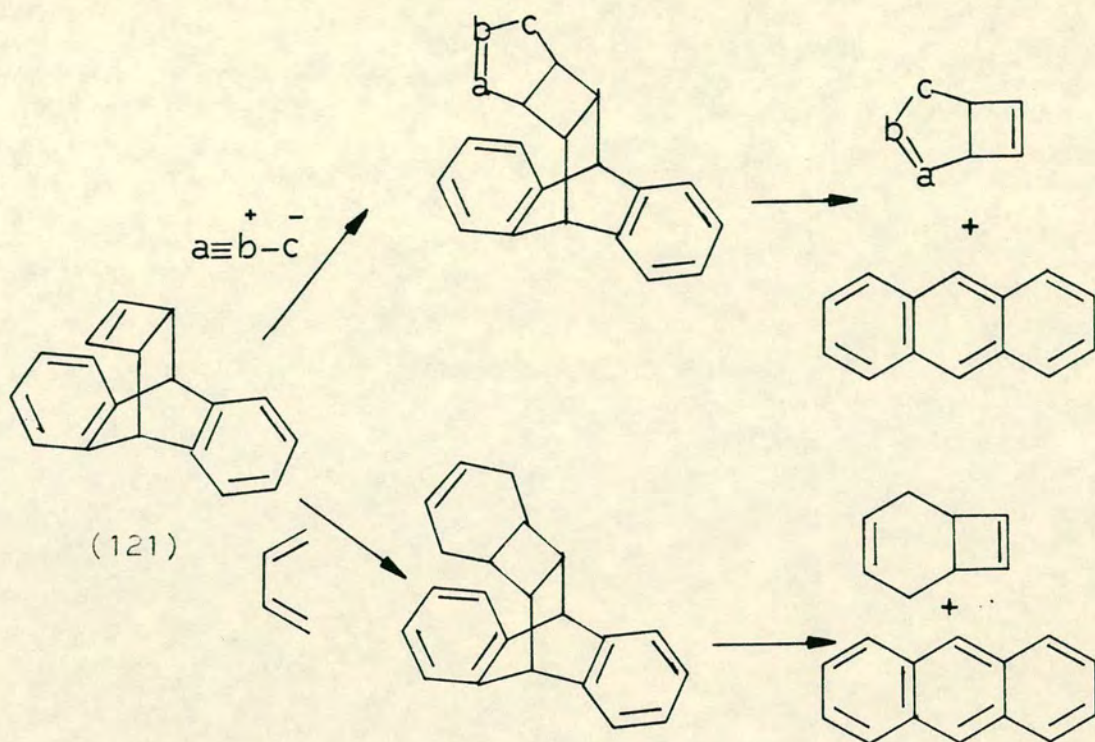
acetylene synthon as its 1,3 dipole adducts (see Table 2). However, in Diels-Alder reactions its ability to act as an acetylene synthon diminishes, and it tends to undergo the retro-Diels-Alder reaction readily, unless, as in the case of the tetracyclone adduct (109), an aromatic molecule can be extruded.

The reaction of cyclobutene anhydride (87) with anthracene was of considerable interest since in principle the adduct (118) could be decarboxylated under oxidative conditions to give cyclobutananthracene (121), a compound with obvious potential as a synthetic equivalent of cyclobutadiene.



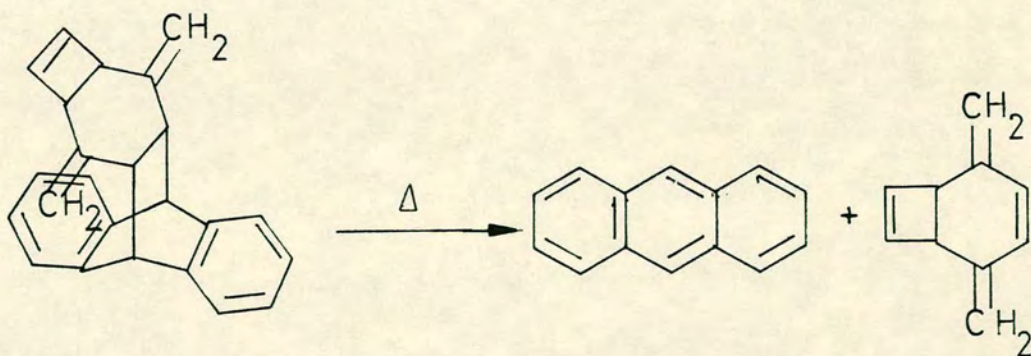
Because of the presence of a strained double bond in (121) this compound is expected to react readily with 1,3-dipolar reagents and dienes to give a variety of adducts (Scheme 31).

As already shown by the decomposition of adducts such as (109) (p.114) loss of an aromatic moiety can provide a large driving force for the thermal cleavage of compounds of



Scheme 31

this type. In this respect, Minter and Fonken⁹⁴ have already shown the use of anthracene as a leaving group (Scheme 32).



Scheme 32

The preparation of (121) and an investigation of its utility as a cyclobutadiene equivalent are described in the next section, following a brief outline of the chemical history of cyclobutadiene itself.

B. Preparation and pyrolysis of some derivatives of
7,8:9,10 dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene

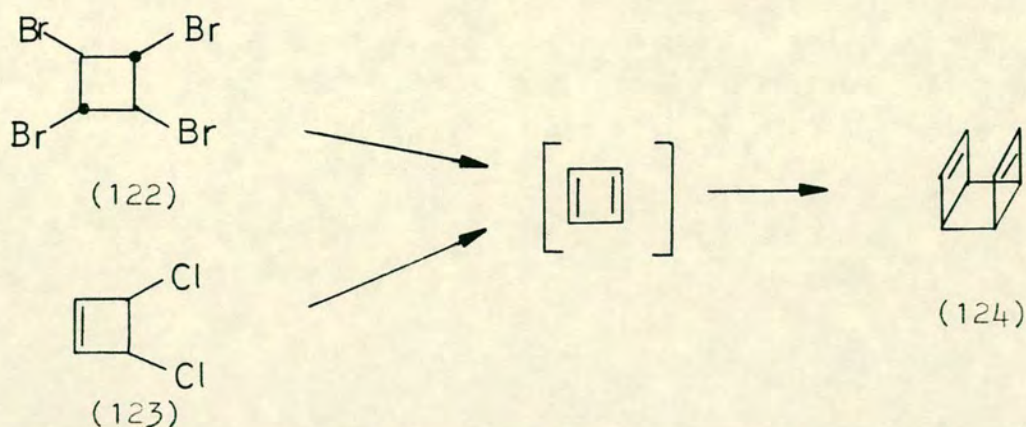
1. General background

In much the same way that acetylene synthons are sought after in synthetic organic chemistry so too are cyclobutadiene synthons. Whereas acetylene synthons are necessary because of the low reactivity of acetylene with other compounds, cyclobutadiene synthons are useful because of the inconvenience involved in the generation of free cyclobutadiene. Cyclobutadiene itself had not been characterised directly until the early 1970's⁹⁵. Evidence of cyclobutadiene's existence as an intermediate in certain reactions was based upon the isolation of a stable product, mainly the dimer of cyclobutadiene, which could be considered a primary or even a secondary transformation product of cyclobutadiene.

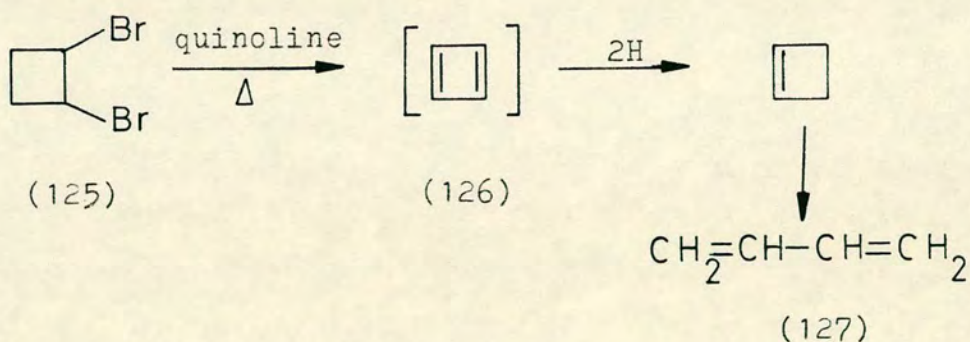
The following is a brief outline of the procedures adopted so far.

(a) Cyclobutadiene

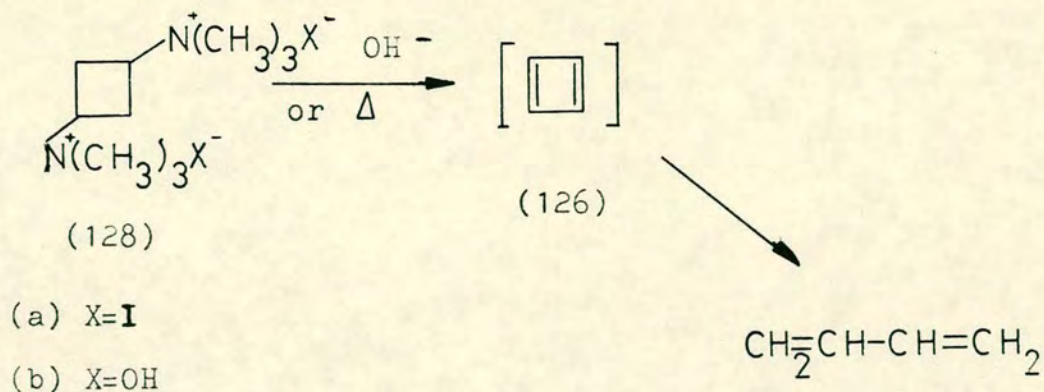
The treatment of all trans-1,2,3,4-tetrabromocyclobutane (122) with lithium amalgam^{96,97} or dechlorination of the 3,4 dichlorocyclobutene (123) with sodium amalgam^{98,99} gave the syn-dimer of cyclobutadiene (124) as the only isolable product.



In a related approach, dehydrohalogenation of 1,2-dibromocyclobutane¹⁰⁰ (125) in boiling quinoline⁸⁵ gave a small amount of butadiene (127) which is believed to arise via the formation of cyclobutadiene (126).

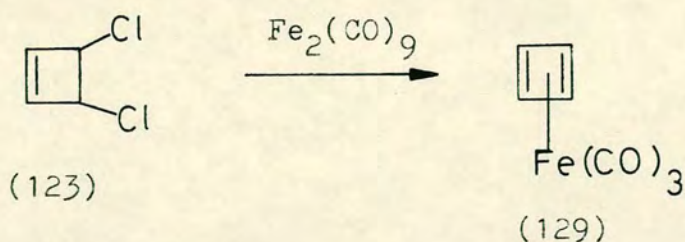


Butadiene was also formed in small yields when 1,3-bis(dimethylamino)cyclobutane dimethiodide (128a) was heated with aqueous potassium hydroxide or with silver oxide suspended in methanol.¹⁰¹ The same product is also formed when solid 1,3-bis(dimethylamino)cyclobutane dimethohydroxide (128b) was subjected to dry pyrolysis.



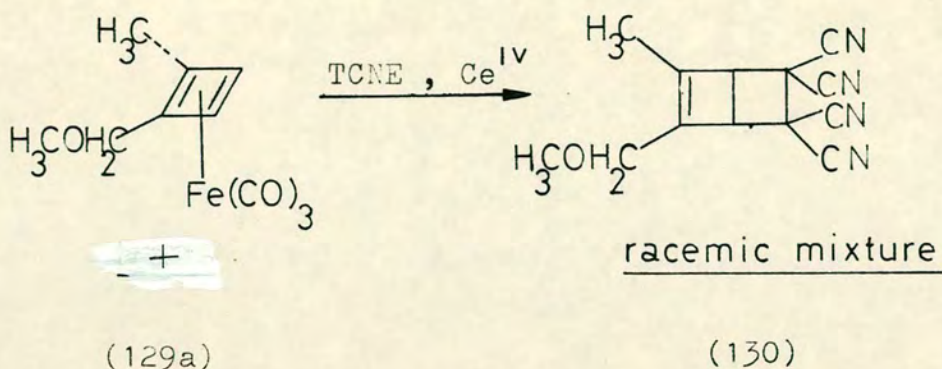
Substituted cyclobutadienes have been generated from substituted acetylenes¹⁰² although cyclobutadiene itself has not been observed from the attempted dimerisation of acetylene. Nonetheless the retro-reaction has been observed on several occasions.

In 1965 Pettit *et al.*¹⁰³ reported the synthesis of the parent cyclobutadiene iron tricarbonyl (129) from 3,4-dichlorocyclobutene (123); since then other methods of synthesis of cyclobutadiene iron tricarbonyl (129) have been made available.^{104,105}

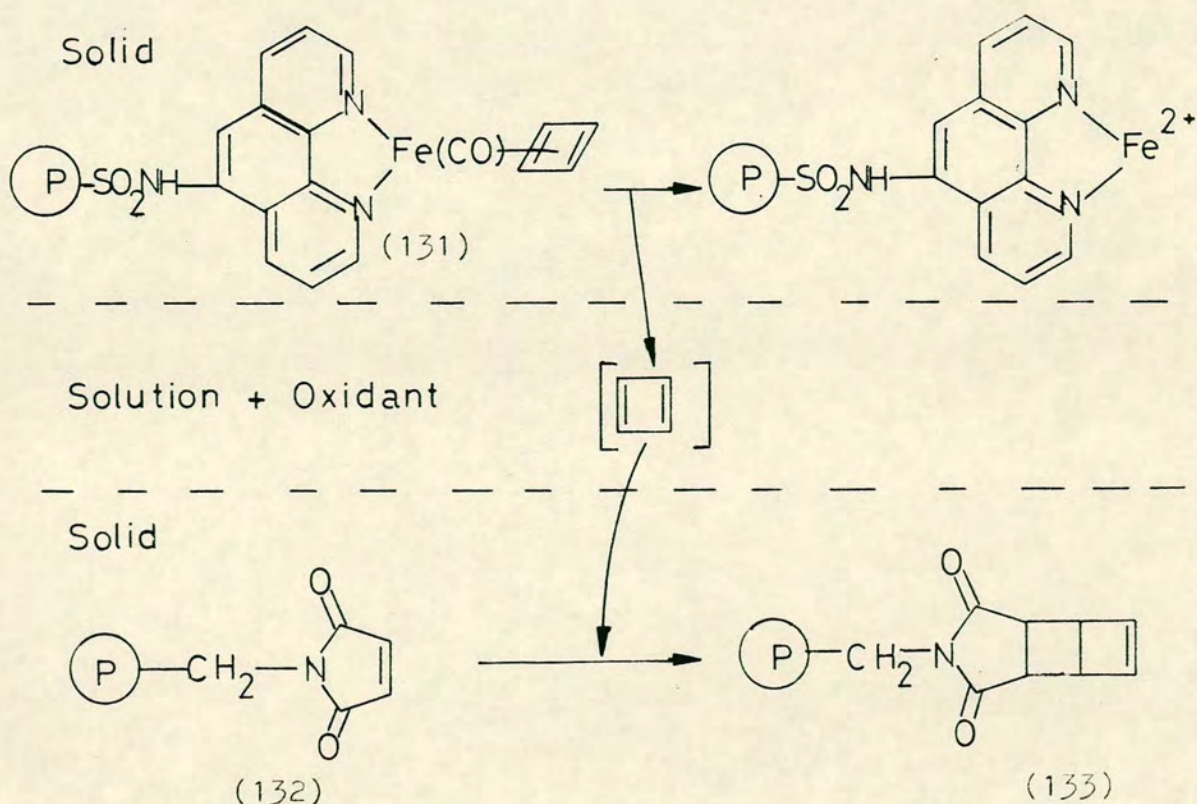


Oxidative treatment of complex (129a) with Ce (IV) in the presence of a dienophile led to formation of adducts (130) which suggested that free cyclobutadiene may have been present as a transient species in the reaction.¹⁰⁷ The proof for

the existence of cyclobutadiene was given by two different groups of workers, who employed optically active derivatives of cyclobutadiene to form a racemic adduct.¹⁰⁷⁻¹⁰⁹

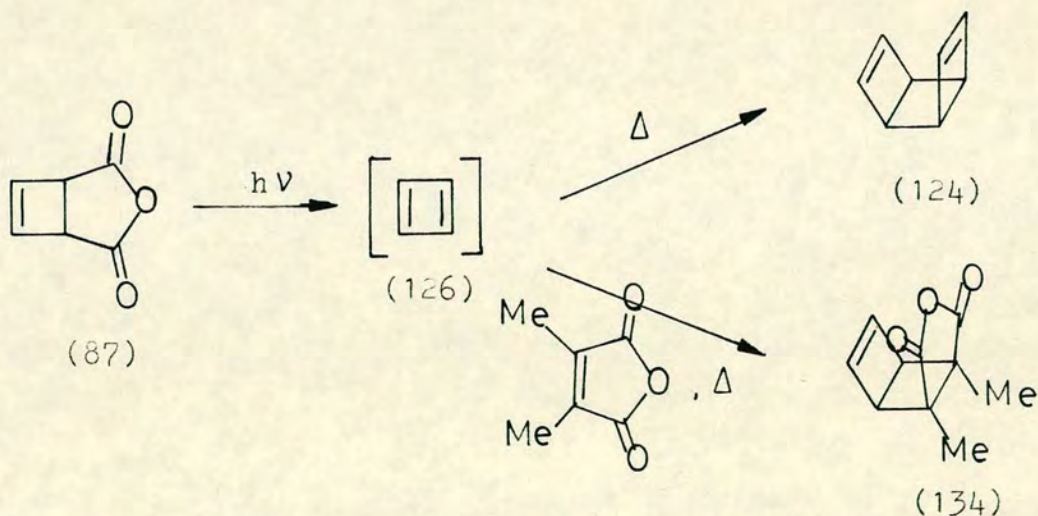


In a novel experiment¹¹⁰ to detect cyclobutadiene, a three phase test was employed. The reagent solution liberated the cyclobutadiene from a polymeric precursor (131) and a second solid phase (132), suspended in the same solution, was used to trap the intermediate as adduct (133), as shown in Scheme 33.

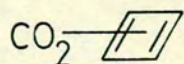


Scheme 33

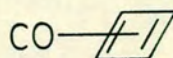
Cyclobutadiene in a 'free state' has been observed from the irradiation of various precursors in a matrix at low temperatures. For example, Maier *et al.*⁹⁵ photolysed compound (87) ^{with} radiation of wavelength 253.7 nm at -196°C using an ether|THF|isopentane matrix to suppress intermolecular dimerisation.¹¹² This produced cyclobutadiene (126), whose formation was deduced by i.r. spectroscopy as evidenced by the presence of both carbon monoxide and carbon dioxide in the matrix. After eight hours of irradiation, followed by thawing of the matrix, dimer (124) was formed in a 9% yield. In the presence of dimethylmaleic anhydride a small amount of adduct (134) could be detected.



In related experiments carried out at 7°K , Maier *et al.*¹¹³ showed that cyclobutadiene was not in fact present in the matrix in a free state but was formed as complexes associated with carbon dioxide (135) and carbon monoxide (136).

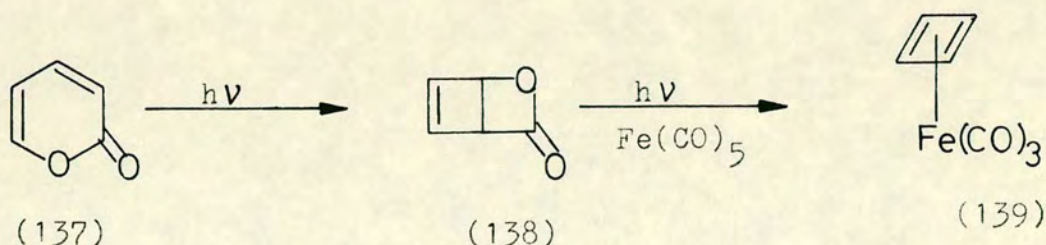


(135)



(136)

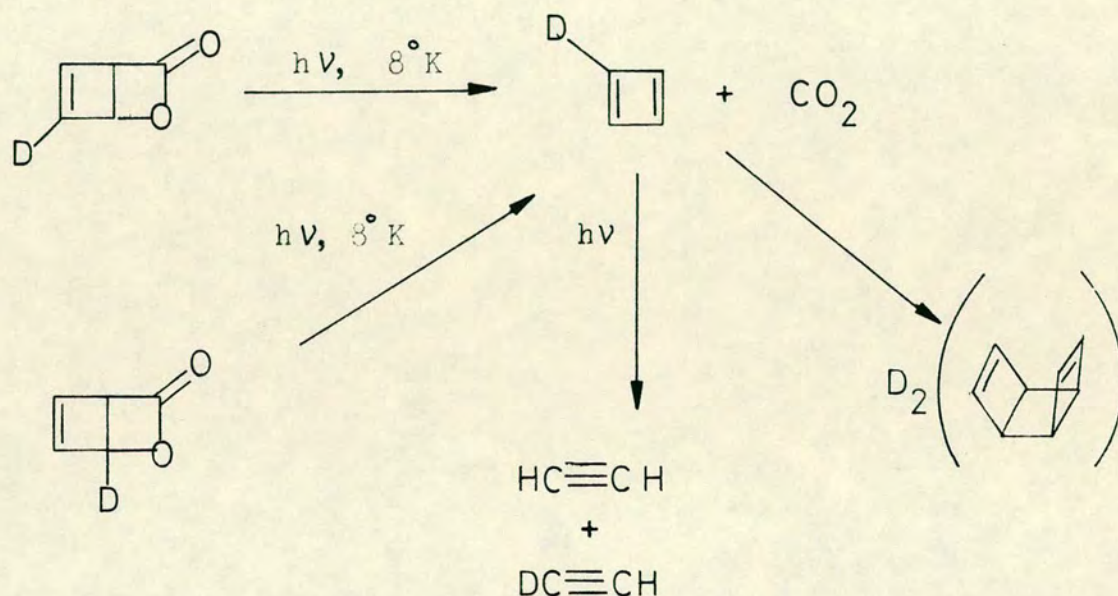
In 1964 Corey *et al.*¹¹⁴ prepared and isolated the lactone (138) from photolysis of α -pyrone (137) and suggested that the removal of carbon dioxide should provide access to cyclobutadiene. Indeed further photolysis of (138) in the



presence of iron pentacarbonyl at -15°C gave the cyclobutene iron tricarbonyl (139); a cobalt complex¹¹⁵ could also be formed by photolysis in the presence of cobalt octacarbonyl.

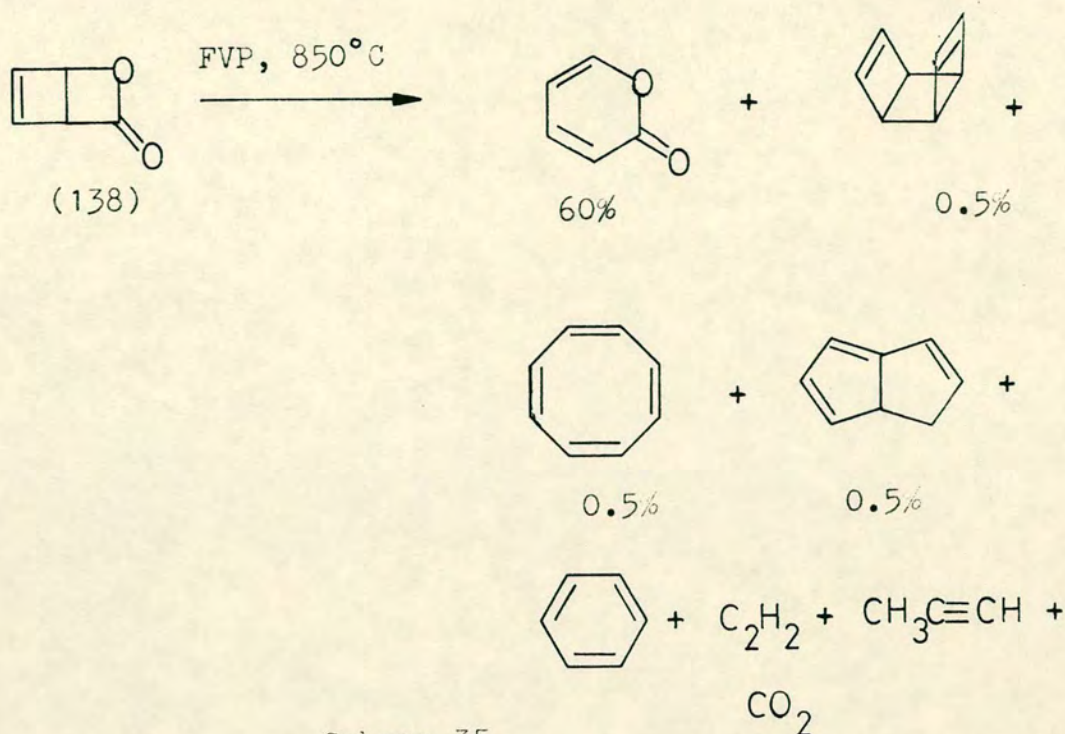
In subsequent experiments evidence was presented that photolysis of the photo-lactone (138) led to the formation of cyclobutadiene and carbon dioxide.¹¹⁶ However Maier *et al.*¹¹³ showed from IR studies that the carbon dioxide functioned as a ligand as found in (135). Kranz *et al.*¹¹⁷ later offered a proof for this observation. On warming the matrix above 35K, while continuing the irradiation, the peaks due to the

cyclobutadiene disappeared to give bands identical to those of acetylene.^{117,118} On warming without irradiation the syn-dimer was formed. Deuterium labelling experiments by Chapman et al.¹¹⁹ left little doubt that cyclobutadiene was present in the complex.

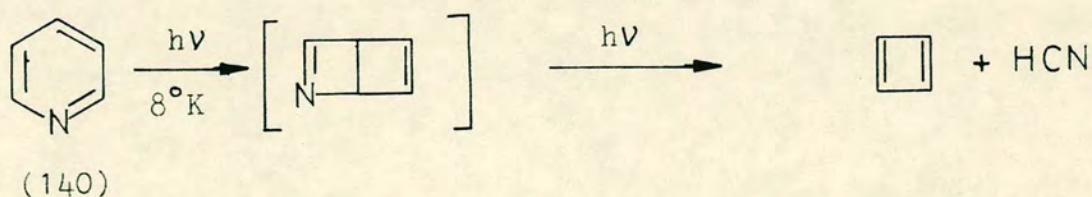


Scheme 34

When the photolactone (138) was subjected to flash vacuum pyrolysis¹²⁴ at 850°C, it afforded a plethora of products which are best rationalised in terms of cyclobutadiene formation.

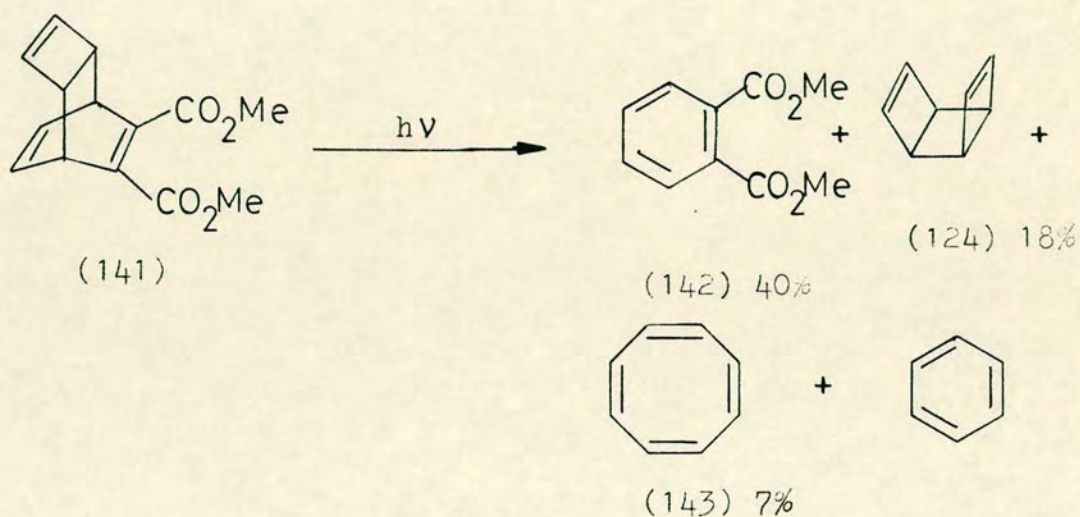


In another low temperature approach, irradiation of a pyridine matrix (140) in argon at 8°K gave hydrogen cyanide and cyclobutadiene.¹¹⁹



Cyclobutadiene has also been implicated in the photolysis of (141),¹²² which is formed by the reaction of cyclooctatetraene with dimethyl acetylene dicarboxylate.¹⁴ After irradiation at 77°K in an ether-isopentane glass, followed by warming of the solution, several products were formed including (142), (124) and (143). This result and the specific formation

of the syn-dimer (124) may arise from the unlikely production of (124) by the initial dimerisation of (141) and its subsequent fragmentation. However, the absence of dimethyl acetylene dicarboxylate implied that dimer (124) was not produced directly from (141), by a retro-Diels-Alder reaction, but from the dimerisation of cyclobutadiene.



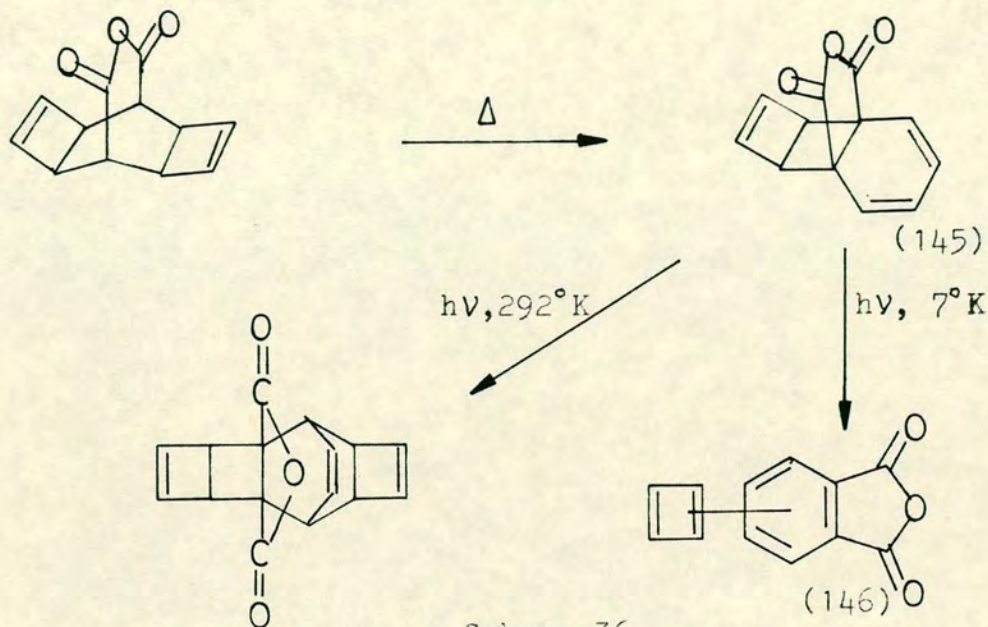
Masamune et al.¹²³ used 2,3-diazabicyclo[2.2.0]hexa-2,5-diene (144) as a cyclobutadiene precursor which gave cyclobutadiene via a retro-Diels-Alder reaction. The exclusive formation



of cyclobutadiene was verified by several independent experiments^{118,122,124} using metal free precursors.

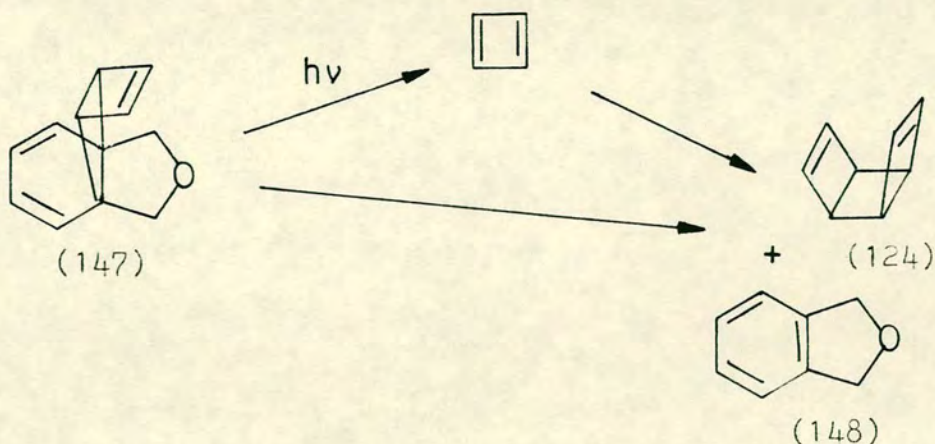
Other experiments included the irradiation of (145) by

Maier et al.¹²⁵ in an argon matrix at 7°K for ten minutes. This reaction gave phthalic anhydride and cyclobutadiene, apparently as a ligand complex (146).



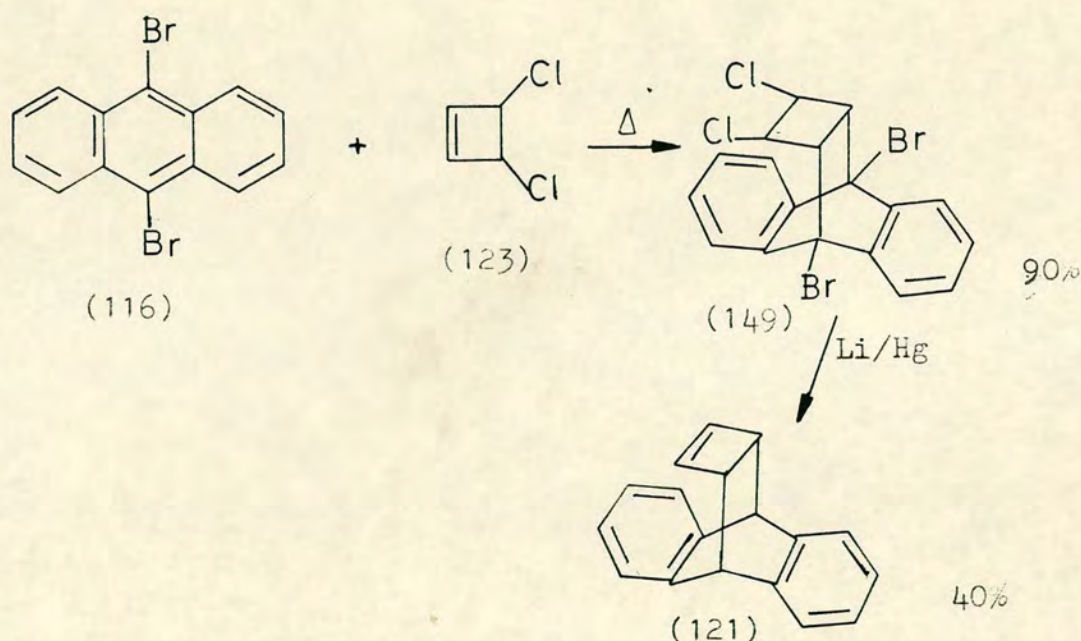
Scheme 36

Finally Masamune et al.¹²⁶ irradiated the compound (147) in deuterated THF at -100°C with 253.7nm radiation to form syn-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene (124) and phthalan (148) exclusively. Indeed compound (147) underwent the most efficient photocleavage of any molecule to date due to its intense absorption in the region of 250-260nm. From UV studies no complex between the cyclobutadiene and phthalan (148) was shown to exist.



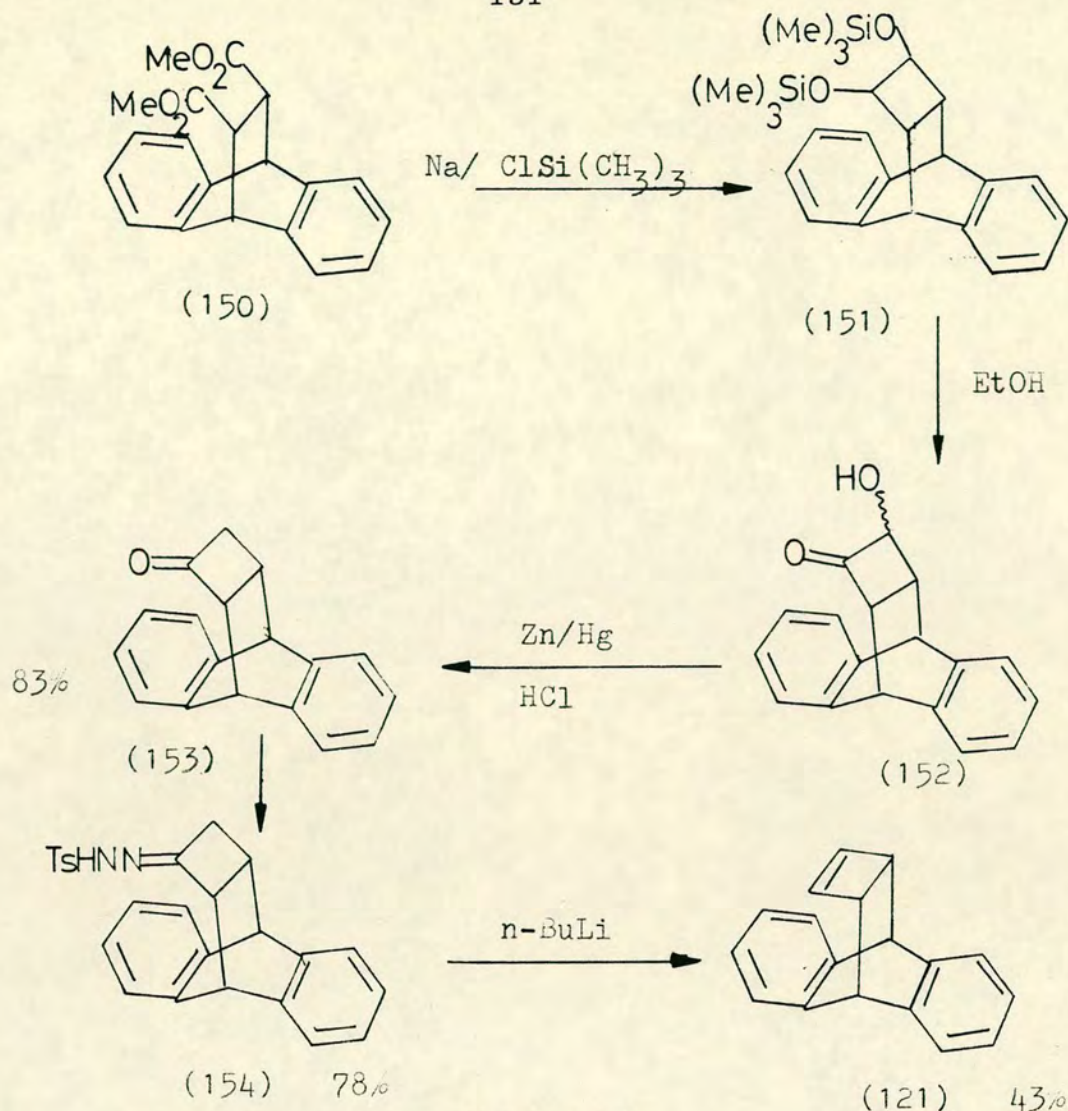
b. 7,8:9,10-Dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene

7,8:9,10-Dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (121), hitherto called cyclobutananthracene, has been prepared previously by two different methods. In 1966 Nenitzescu et al.⁷² carried out the Diels-Alder cycloaddition of 9,10-dibromoanthracene (116) with cis-3,4-dichlorocyclobutene (123) to give the adduct (149) which was reduced by lithium amalgam to give cyclobutananthracene (121) in 36% overall yield, (Scheme 37).



Scheme 37

In the other method, Sugihara et al.⁷³ prepared cyclobutananthracene by the route shown in Scheme 38. This involved the addition of maleic anhydride to anthracene³⁷, followed by conversion of the derived adduct into the dimethyl ester (150). The ester gave the siloxy derivative (151) on treatment with sodium in the presence of trimethylchlorosilane.¹²⁷ Hydrolysis of the latter with ethanol resulted in the formation

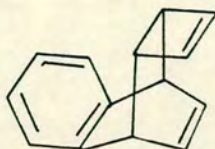


Scheme 38

of the acyloin (152) which was reduced with zinc amalgam and 4N HCl to give the cyclobutanone (153). Conversion of (153) into its *p*-toluenesulphonylhydrazone (154) followed by reaction with excess *n*-butyllithium in diglyme gave the desired alkene (121) in 28% overall yield.

Both of the methods have certain disadvantages. Nenitzescu's⁷² approach used the relatively expensive 9,10-dibromoanthracene and the very expensive 3,4-dichlorocyclobutene; it also involved an inconvenient lithium amalgam reduction. The obvious disadvantage with Sugihara's⁷³ route is the length of the multi-stage preparation, which is not only time consuming but led to an overall lower yield.

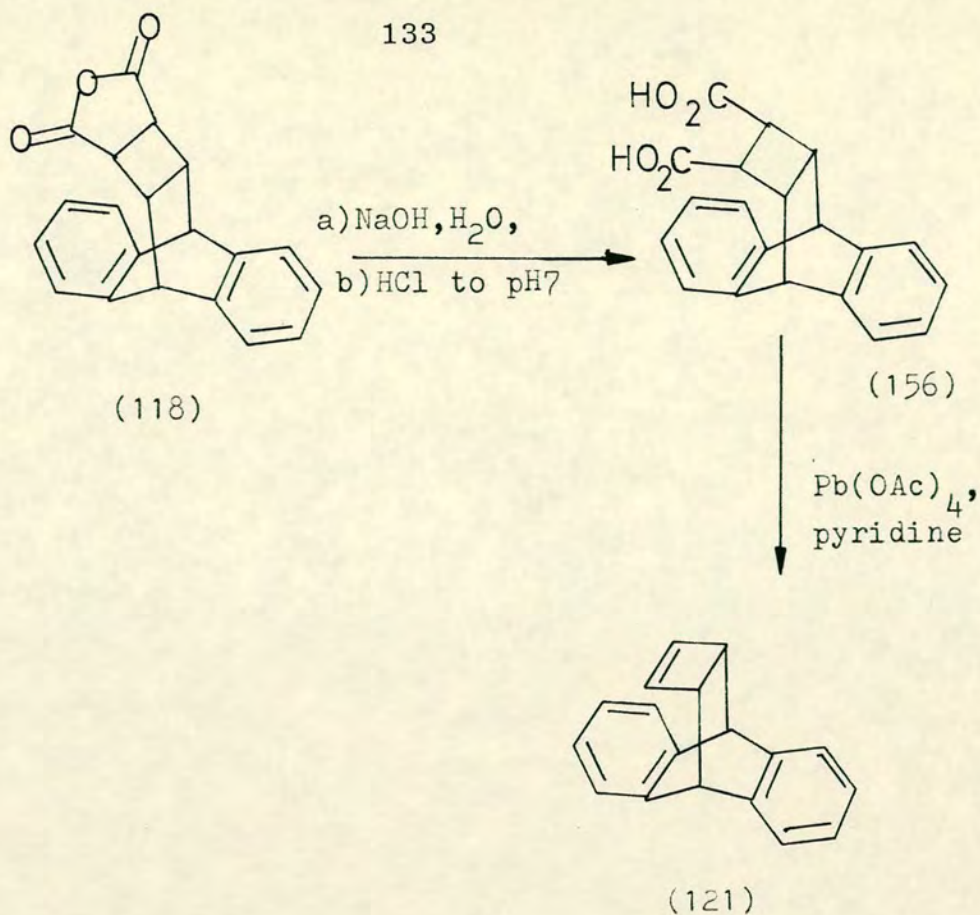
Nonetheless it should be noted that Sugihara's method was primarily devised for the synthesis of syn-7,8-benzotricyclo-[4.2.2.0^{2,5}]deca-3,7,9-triene (155) which cannot be obtained by Nenitzescu's method.



(155)

2. Preparation and pyrolysis of 7,8:9,10-dibenzotricyclo-[4.2.2.0^{2,5}]deca-3,7,9-triene

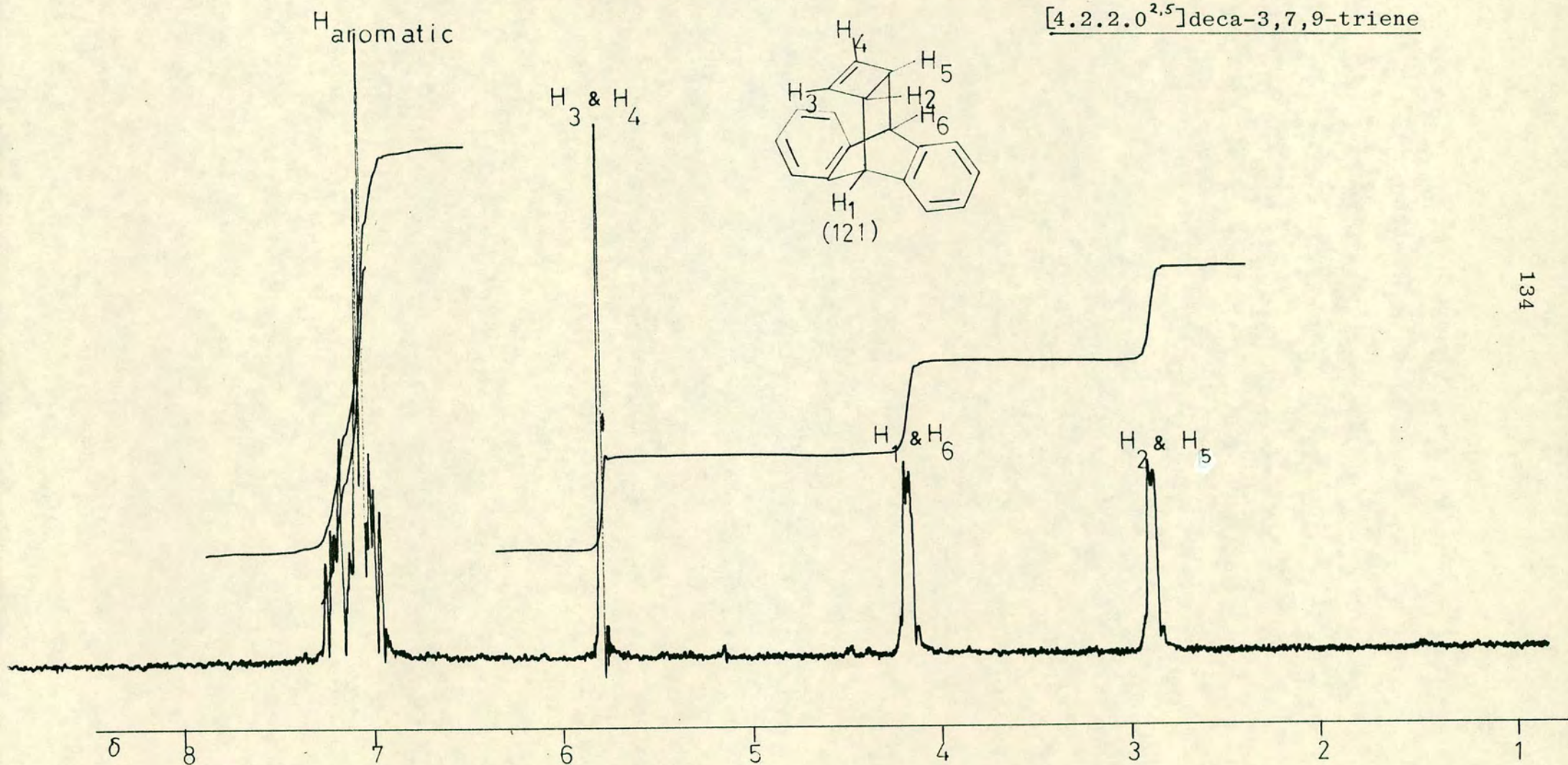
The method devised for the preparation of cyclobutananthracene (121) utilised the Diels-Alder cycloaddition of cyclobutene anhydride (87) with anthracene, a reaction that occurred in good yield, as discussed previously. The adduct was then converted into the diacid (156) which underwent a facile oxidative decarboxylation using lead tetraacetate^{9,10} in pyridine to give the desired compound (121) in a 32% yield. This yield is comparable to that from Nenitzescu's⁷² preparation but the starting materials involved are certainly less expensive and to date represents the most convenient preparation of cyclobutananthracene.

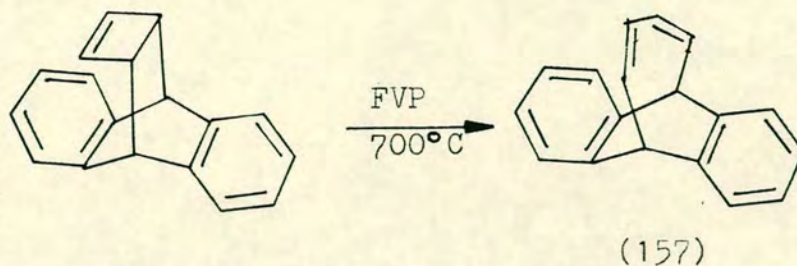


It was envisaged that under F.V.P. conditions anthracene and cyclobutadiene might be formed due to the retro-Diels-Alder reaction of cyclobutananthracene. Of course, only anthracene could be positively identified under these conditions but its presence would indicate cyclobutadiene extrusion. However no evidence for the formation of anthracene was found. Instead under flash vacuum pyrolytic conditions at 700°C cyclobutananthracene gave the ring expanded product, 9,10-butadiene-9,10-dihydroanthracene (157), in virtually quantitative yield. A similar result was obtained by Nenitzescu et al.⁷⁴ previously, but interestingly thermolysis of (121) in chloroform at 165°C in a sealed tube showed no evidence of rearrangement to form (157).

Fig 4 ^1H -n.m.r. spectrum of 7,8:9,10-dibenzotricyclo-

[4.2.2.0^{2,5}]deca-3,7,9-triene

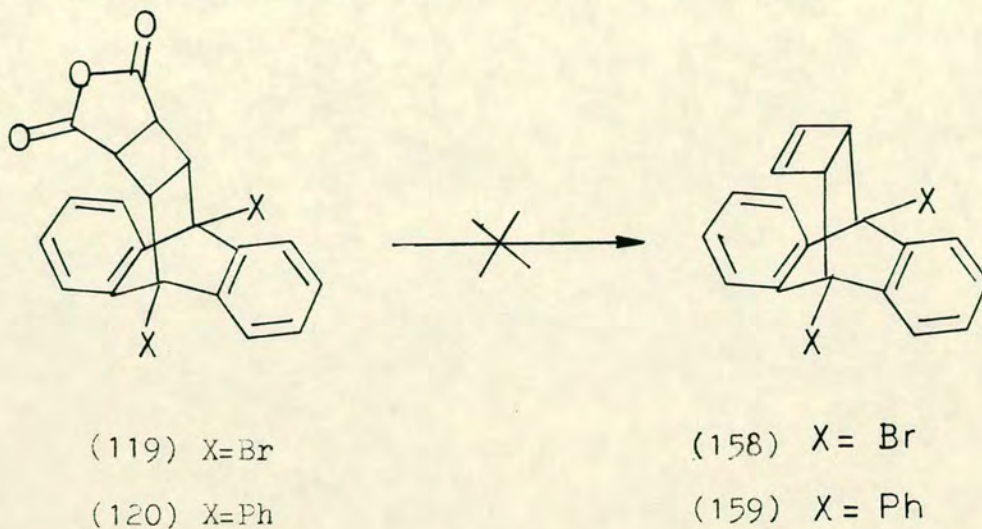




3. Attempted synthesis of 9,10-disubstituted 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes

In related experiments it was considered that the presence of substituents at the 9,10-positions of the cyclobutananthracene (121) might provide sufficient steric hindrance, or else, electronically induce the thermolysis of (121) to undergo an alternative fragmentation involving extrusion of cyclobutadiene and the formation of a 9,10-disubstituted anthracene. For this reason both 9,10-dibromoanthracene (116) and 9,10-diphenylanthracene (117) were reacted with cyclobutene anhydride (87) in boiling toluene to give the adducts (119) and (120) respectively. In the case of (120) the generation of the diacid proved impossible because the compound was insoluble in an aqueous medium and apparently inert to base. By comparison the dibromo-anthracene adduct (119) gave the diacid in good yield, but the oxidative bis-decarboxylation with lead tetraacetate led to the recovery of the starting anhydride (116).

In this respect it is worth noting that anhydride formation has been observed in the bis-decarboxylation of several bicyclic acids.^{128,129}

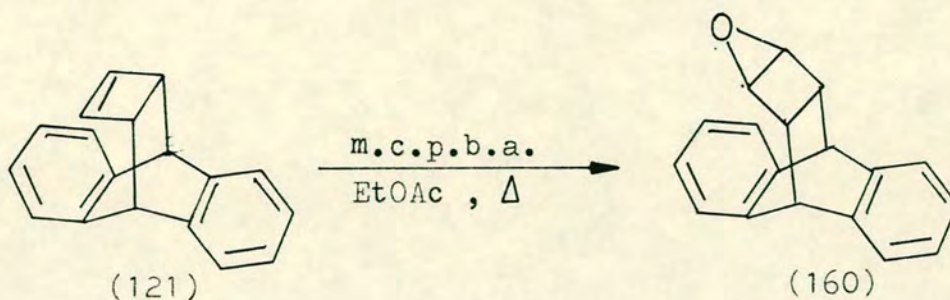


Since the formation of cyclobutadiene could not be obtained from the pyrolysis of (121) nor could the alkene derivatives (158) or (159) be synthesised, it was speculated that cyclobutananthracene (118) might serve as a useful cyclobutadiene synthon.

4. Preparation and pyrolysis of the epoxide of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene

Cyclobutananthracene (121) reacted readily with several 1,3-dipoles but the derivative which led to its investigation as a cyclobutadiene synthon was its epoxide (160). This could be prepared in 85% yield by reaction with *m*-chloroperoxybenzoic acid in boiling ethyl acetate. The ¹H-n.m.r. spectrum of the epoxide (160) was similar to that of the cyclobutan-

thracene (121), with the exception that the peak at $\delta 5.84$



corresponding to the olefinic protons had disappeared to give rise to the protons neighbouring the epoxide, which appeared in the spectrum at $\delta 3.30$ as a multiplet (see fig.5 later).

Heating of the epoxide (160) in a solution of d-chloroform in a sealed tube at 165°C for seven days resulted in no change of structure, which gives some indication of the epoxide's thermal stability. When the epoxide was pyrolysed under F.V.P. conditions at 550°C it gave both furan and anthracene in yields of 85% and 91% respectively. This was not an unexpected result since the formation of both of these compounds provide a substantial driving force for the reaction. Indeed furan

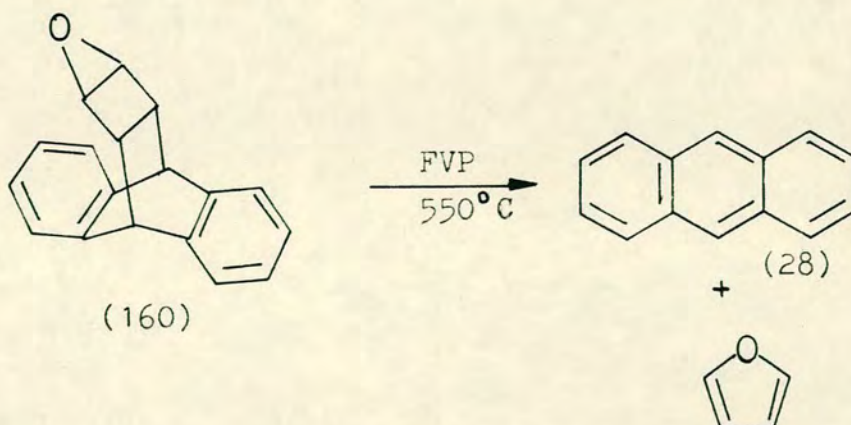
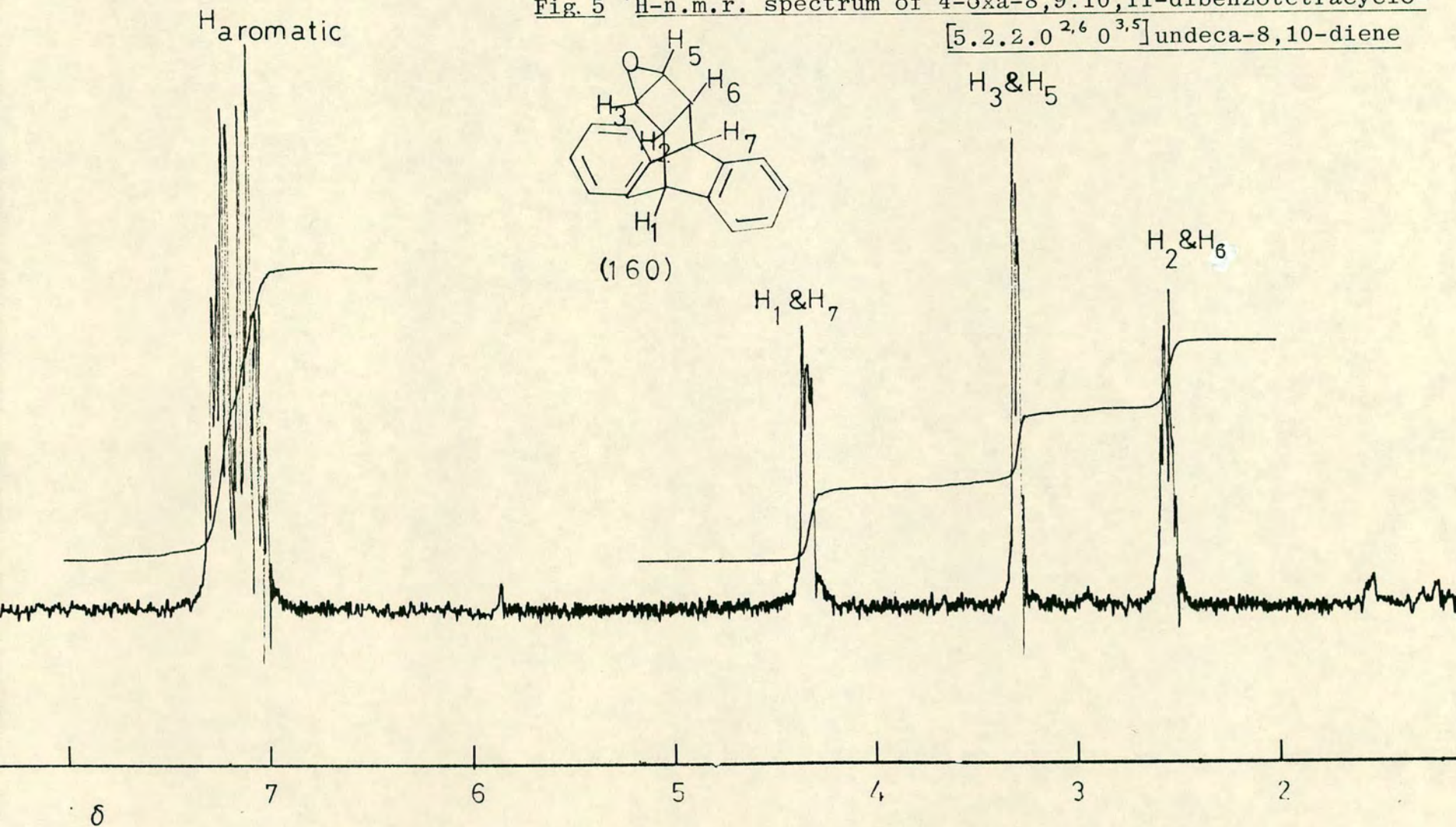


Fig. 5 ^1H -n.m.r. spectrum of 4-oxa-8,9:10,11-dibenzotetracyclo-
 $[5.2.2.0^{2,6}.0^{3,5}]$ undeca-8,10-diene

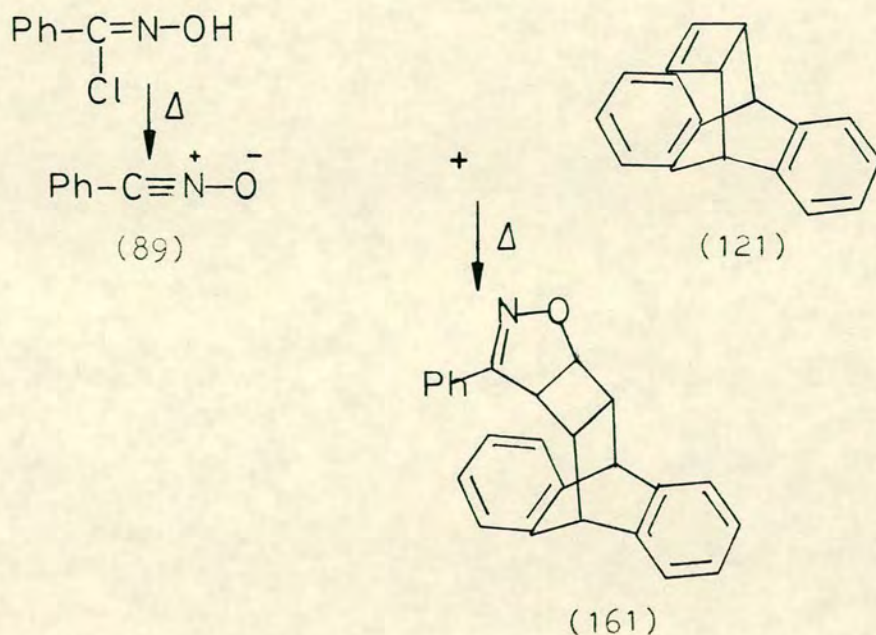


extrusion had been reported to occur readily in the case of several compounds.¹³⁰ This F.V.P. experiment showed that cyclobutanthalracene (121) could serve as a cyclobutadiene equivalent. In this way it was envisaged that reaction of (121) with various cycloadducts followed by pyrolytic extrusion of anthracene might provide a useful method of forming a series of cyclobutadiene adducts.

In general, reactions of cyclobutadiene are difficult to carry out due to its transient nature and the nature of the conditions in which it is generated in a free state.¹²⁶

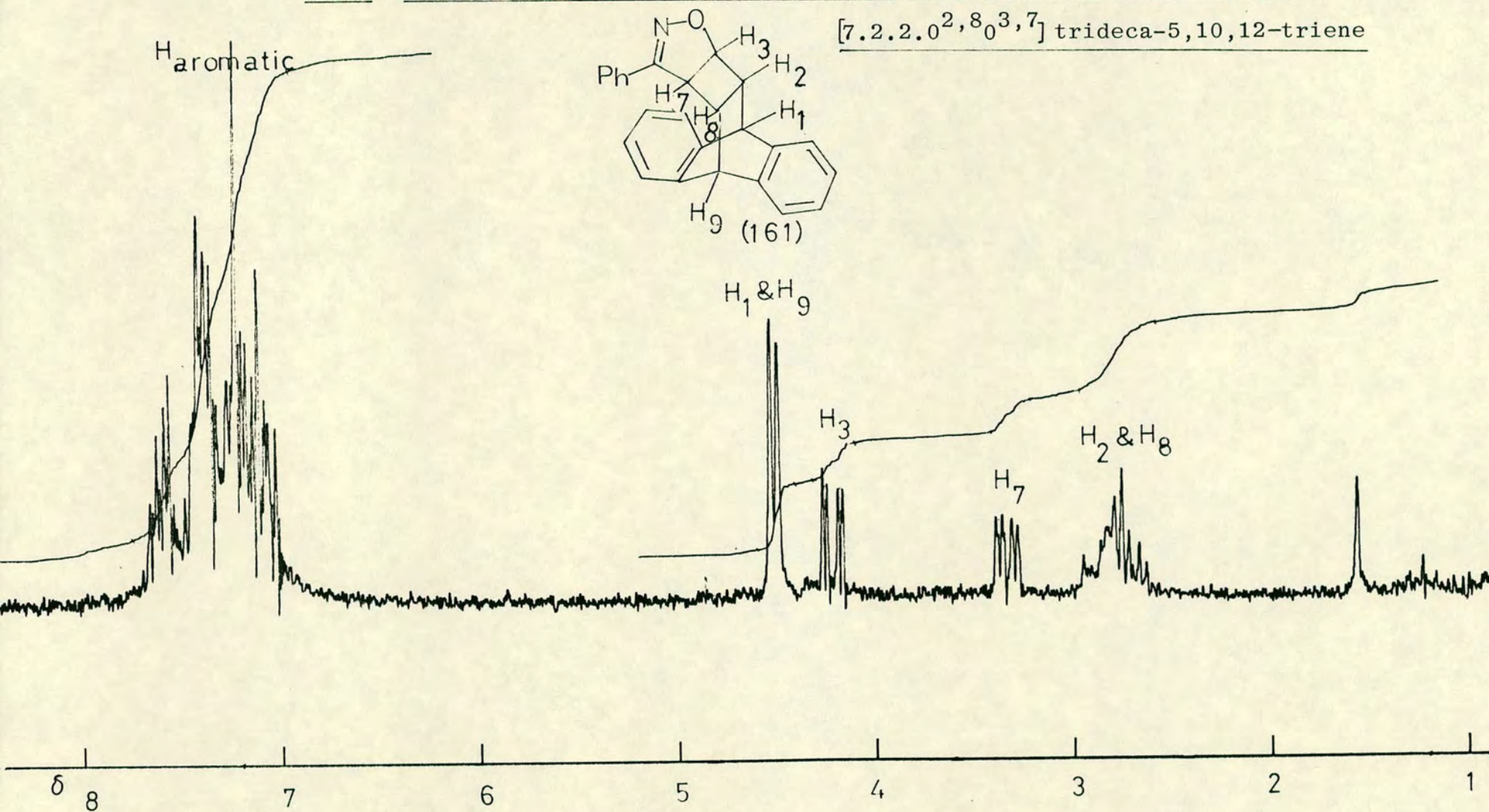
5. Preparation and pyrolysis of 1,3 dipole adducts of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene

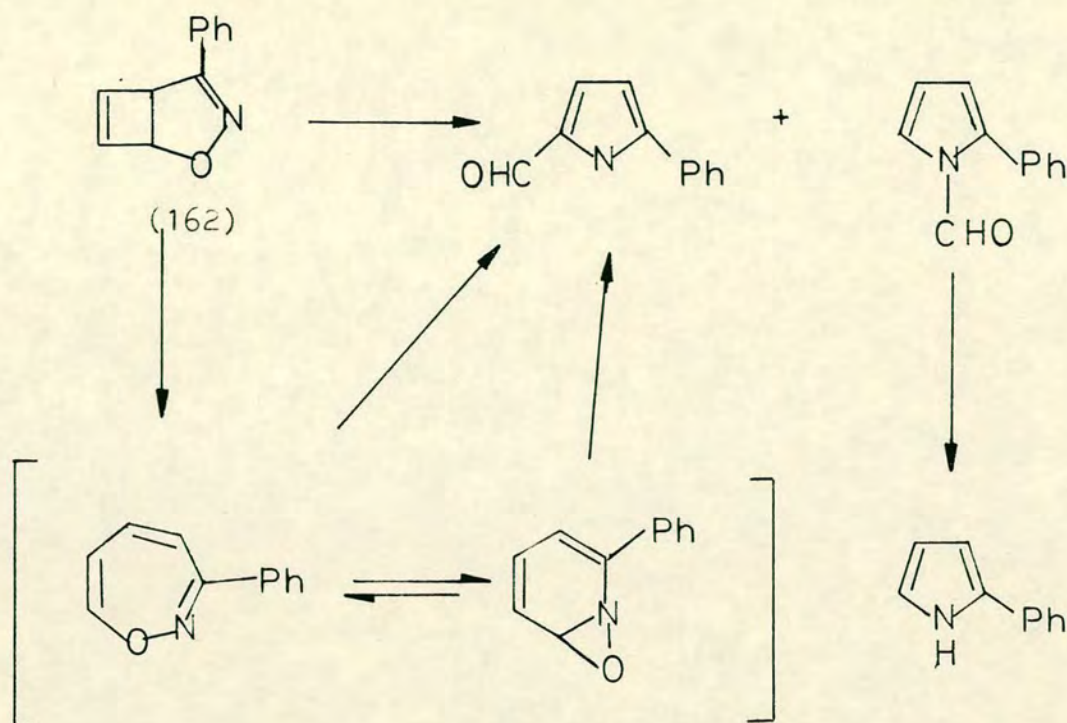
The reaction of cyclobutanthalracene (121) with benzonitrile oxide (89), formed by thermolysis of the corresponding hydroximoylchloride, in boiling toluene gave the adduct (161) in 79% yield. Evidence for the adduct (161) was clearly given



by its analytical and spectroscopic data; the ^1H -n.m.r. spectrum was particularly characteristic with the protons on C(3) and C(7) split identically (dd) and with the C(3)H, next to the O, downfield of C(7)H. It was assumed that pyrolysis of (161) would result in retro-reaction, similar to that observed with the epoxide (160), resulting in loss of anthracene and the formation of 4-phenyl-2-oxa-3-azabicyclo-[3.2.0]hepta-3,6-diene (162). In the event, the pyrolysate from (161) at 625°C was obtained as a yellow solid at -198°C which gradually turned into a purple liquid when warmed to room temperature on contact with air. The ^1H -n.m.r. spectrum of the pyrolysate showed that anthracene was a major component but no evidence could be found for the desired product (162), although the spectrum revealed the presence of an olefinic double bond as a distinctive triplet at $\delta 5.16$ (see fig. 7). Detailed analysis of the spectrum ruled out the possibility that (162) had formed and undergone a thermal rearrangement during pyrolysis in keeping with the observation of Mukai et al.¹¹ shown in Scheme 39.

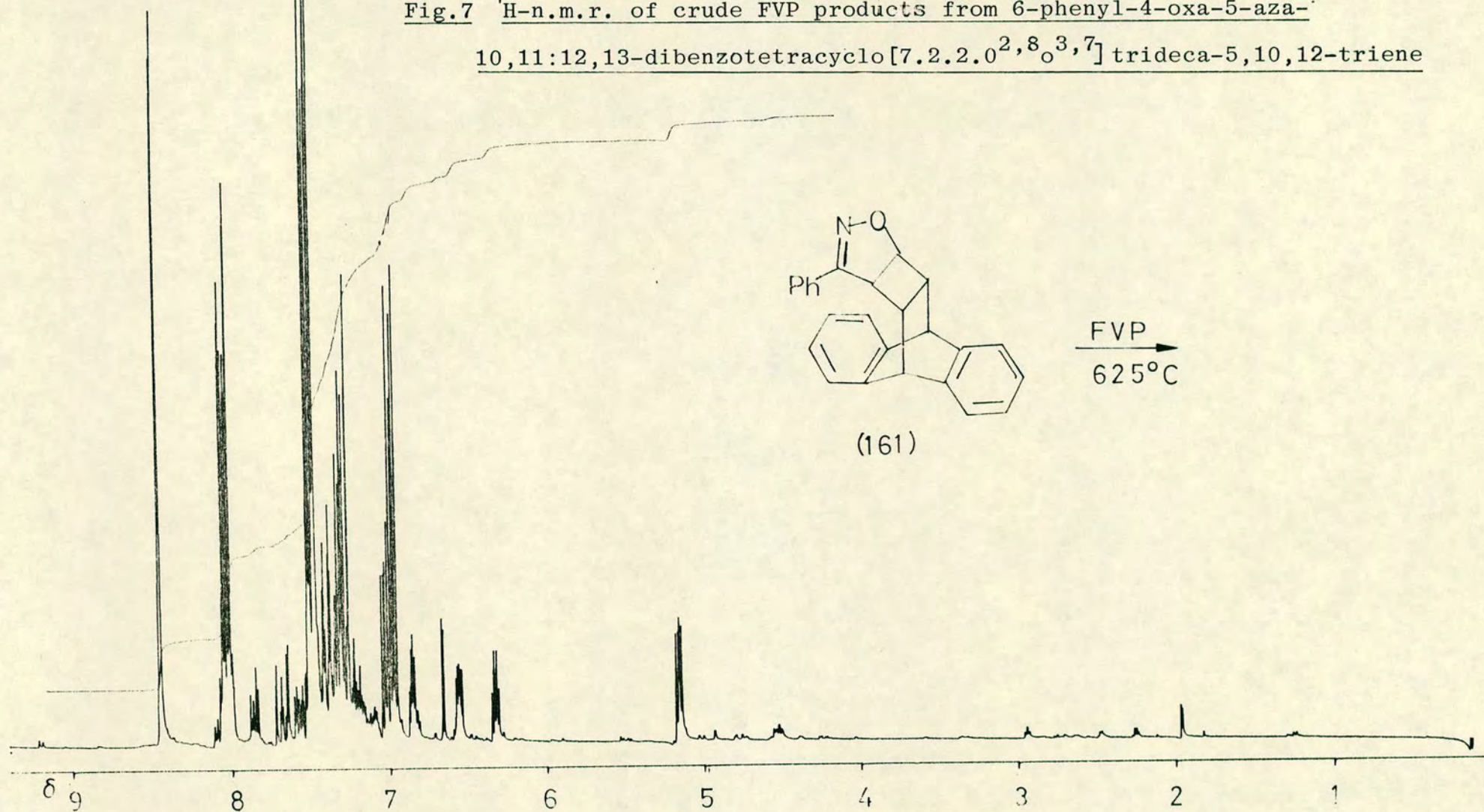
Fig.6 ^1H -n.m.r. of 6-phenyl-4-oxa-5-aza-10,11:12,13-dibenzotetracyclo-
 $[7.2.2.0^{2,8}0^{3,7}]$ trideca-5,10,12-triene

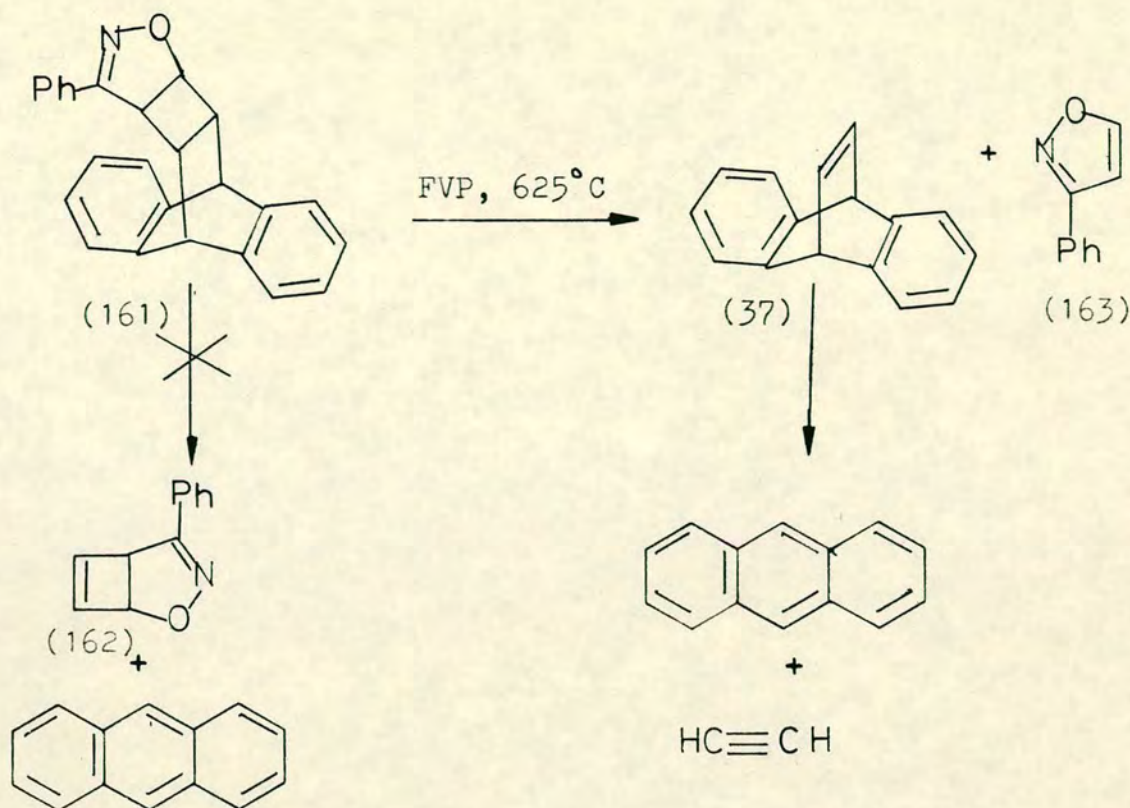


Scheme 39

This was finally verified by g.l.c.-m.s. analysis of the pyrolysate which showed that thermal fragmentation had not followed the expected path, Scheme 39, as evidenced by the presence of a product with a parent ion peak at m/z 204. This was subsequently identified as dibenzobarrelene (37) which also accounted for the characteristic triplet of the olefinic protons at δ 5.16 in the ^1H -n.m.r. spectrum. G.l.c.-m.s. also revealed the presence of another product, with a parent ion peak at m/z 145, indicative of 3-phenylisoxazole (163). This compound was eventually isolated from the pyrolysate and positively identified by its ^1H -n.m.r. spectrum which showed two very characteristic doublets at δ 6.65 and δ 8.84 due to the coupling of the olefinic protons. The formation of all three compounds from the pyrolysis of (161) was confirmed by g.l.c. comparison with authentic samples.

Fig.7 ^1H -n.m.r. of crude FVP products from 6-phenyl-4-oxa-5-aza-
10,11:12,13-dibenzotetracyclo[7.2.2.0^{2,8}.0^{3,7}] trideca-5,10,12-triene



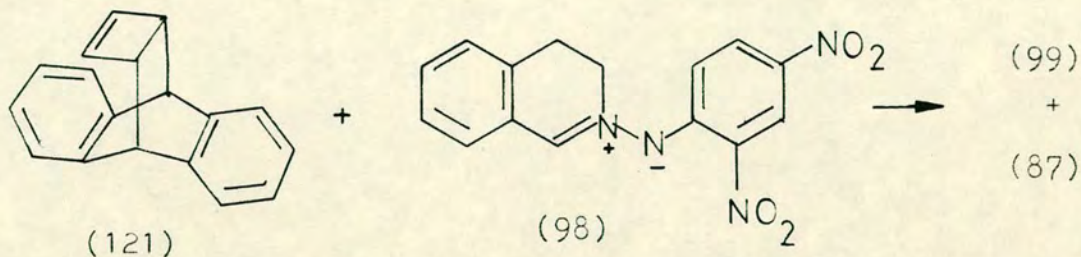


It is apparent from the formation of these products that in this reaction cyclobutananthracene (121) had not served as a cyclobutadiene synthon as expected. Instead, an alternative fragmentation had occurred in which it acted as an acetylene equivalent to give 3-phenylisoxazole (163) and dibenzobarrelene (37), which subsequently underwent partial decomposition to form acetylene. Acetylene was not identified in the pyrolysate but the partial decomposition to acetylene and anthracene was verified by the pyrolysis of an authentic sample of dibenzobarrelene. In this case, the formation of the isoxazole (163) was preferred to that of 4-phenyl-2-oxa-3-azabicyclo[3.2.0]hept-3,6-diene (162) because of the greater stability of the 5-membered ring.

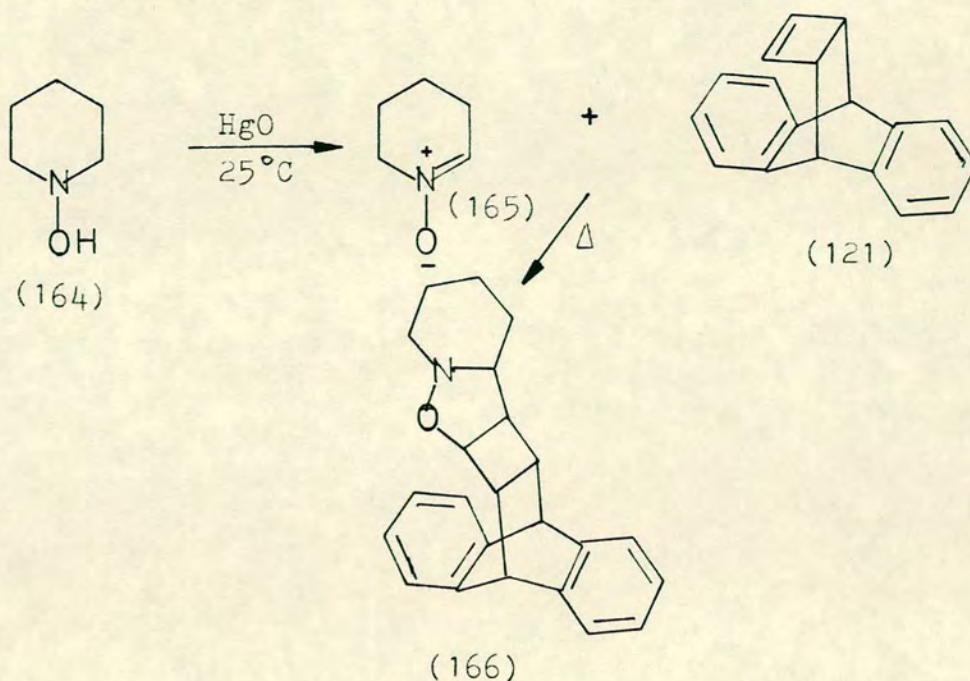
The corresponding reaction of cyclobutananthracene (121) with diphenylnitrile imine (101) proved unsuccessful, as

evidenced by the ^1H -n.m.r. spectrum of the reaction mixture which showed mainly starting alkene was present.

As with cyclobutene anhydride the azomethine imine (98) dimerised in preference to reaction with cyclobutanthalracene (121).



In contrast to the foregoing reaction 1-piperidine 1-N-oxide (165), which was prepared from N-hydroxypiperidine (164) by the method of Kakisawa *et al.*⁷⁵ as shown in Scheme 40, underwent smooth cycloaddition with cyclobutanthalracene (121) in boiling toluene to give the expected adduct (166) in 72% yield.



Scheme 40

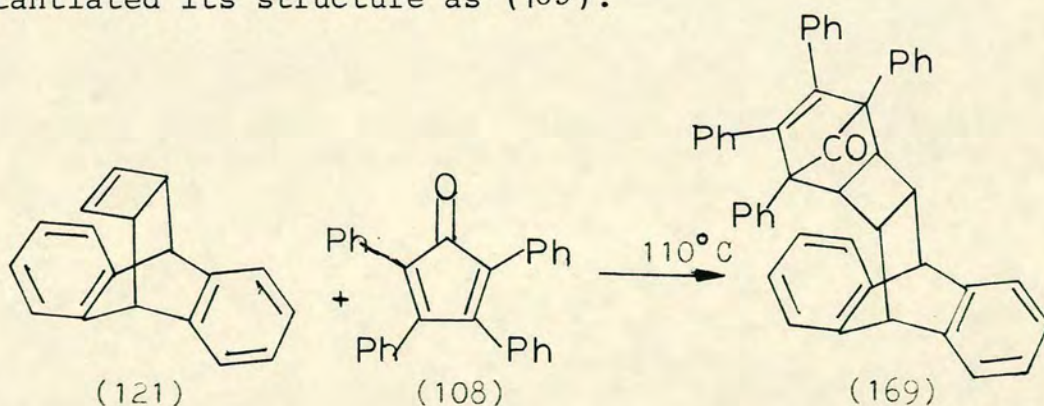
The ^1H -n.m.r. spectrum of the product was extremely complicated, especially in the aliphatic region and could not be properly resolved, but elemental analysis and its mass-spectrum were consistent with the assigned structure. Because the adduct (166) decomposed readily on alumina and silica it was purified by successive recrystallisation. The only identifiable product from column chromatography was cyclobutanthalracene (121). The thermal instability of the adduct (166) was also apparent from pyrolysis studies. When subjected to F.V.P. at 625°C decomposition occurred to give a crude pyrolysate from which anthracene (72%) was obtained. Some dibenzobarrelene was observed in the ^1H -n.m.r. spectrum of the pyrolysate but could not be separated. A volatile red liquid was also obtained which decomposed to a brown liquid on warming and exposure to air and, when purified by preparative t.l.c., gave a compound which defied identification. According to ^1H -n.m.r. spectroscopy it was aromatic in nature while its mass spectrum showed a parent ion peak at m/z 362. Significantly the ^1H -n.m.r. spectrum of the purified compound did not compare with peaks in the spectrum of the pyrolysate prior to chromatography. From this result it would seem that a facile decomposition or rearrangement of the initial products of the pyrolysis occurred during the work-up.

Unlike the epoxide (160), none of the adducts formed with cyclobutanthalracene (121) gave any indication of cyclobutanthalracene acting as a cyclobutadiene synthon under F.V.P. conditions. The adduct (163), formed with phenylisocyanide oxide, underwent F.V.P. in such a way as to show that cyclobutanthalracene acted as an acetylene synthon. In fact, from analysis of the

F.V.P. products from adducts (161) and (166) it would appear that the molecules fragment to give dibenzobarrelene which, in turn, fragments to anthracene and acetylene. In both systems a 5-membered 6π ring compound, dibenzobarrelene and anthracene are formed.

6. Preparation and pyrolysis of the Diels-Alder adducts of 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene

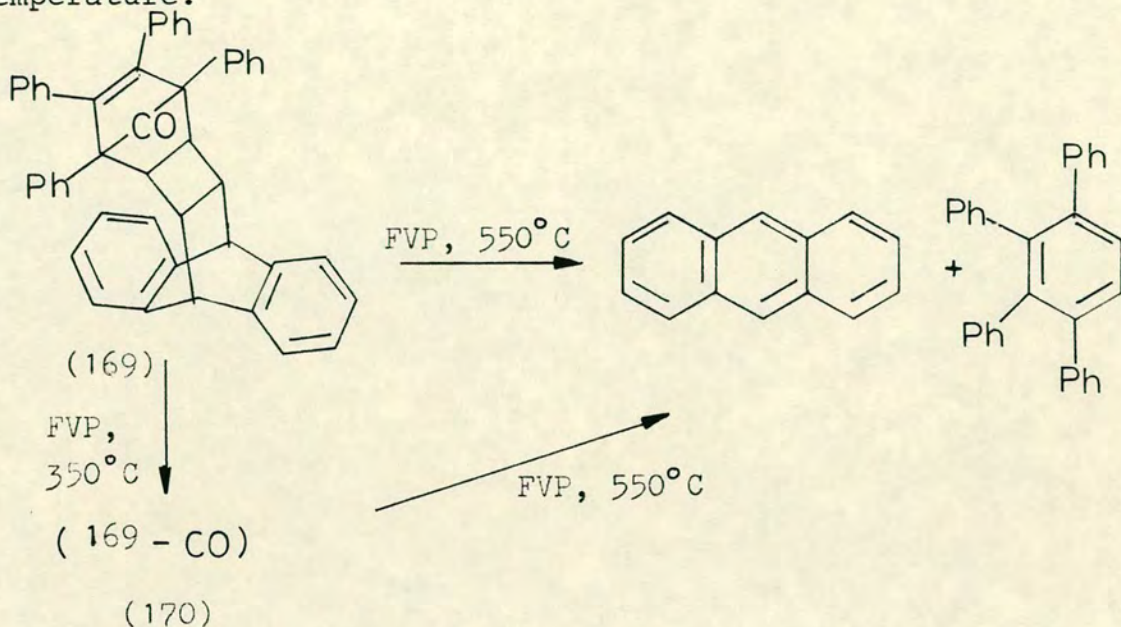
As with other strained olefins, cyclobutananthracene (121) readily underwent Diels-Alder cycloaddition with tetraphenylcyclopentadienone (tetracyclone) (108) in boiling toluene to give a colourless solid in 63% yield. Owing to its insolubility in virtually all solvents, no n.m.r. spectroscopic details could be obtained, but after purification by sublimation, elemental analysis, mass spectroscopy and infrared spectroscopy substantiated its structure as (169).



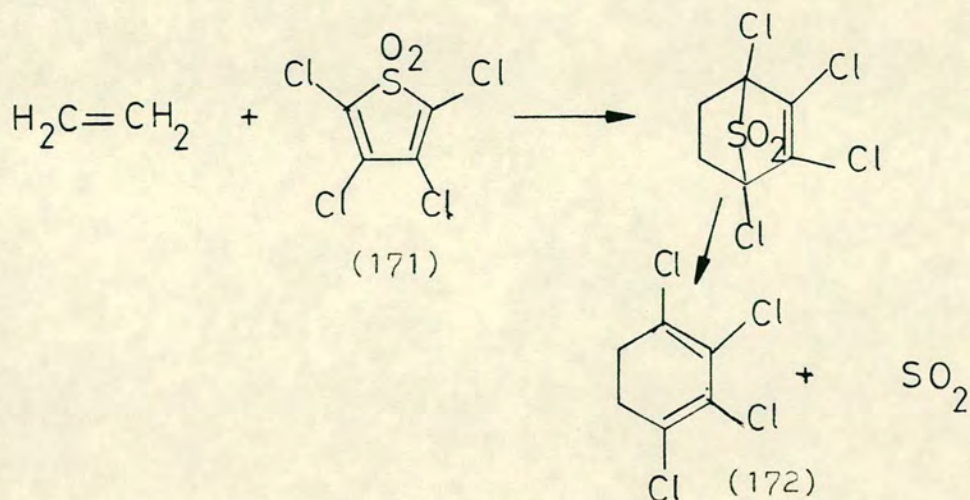
Pyrolysis of the adduct (169) under F.V.P. conditions at 350°C gave a colourless solid (83% yield) whose i.r. spectrum showed no carbonyl absorption, in keeping with structure (170)*. Further pyrolysis of (170) at 550°C resulted in

* Further discussion of the tetracyclone adducts shall continue collectively in Section E.4.

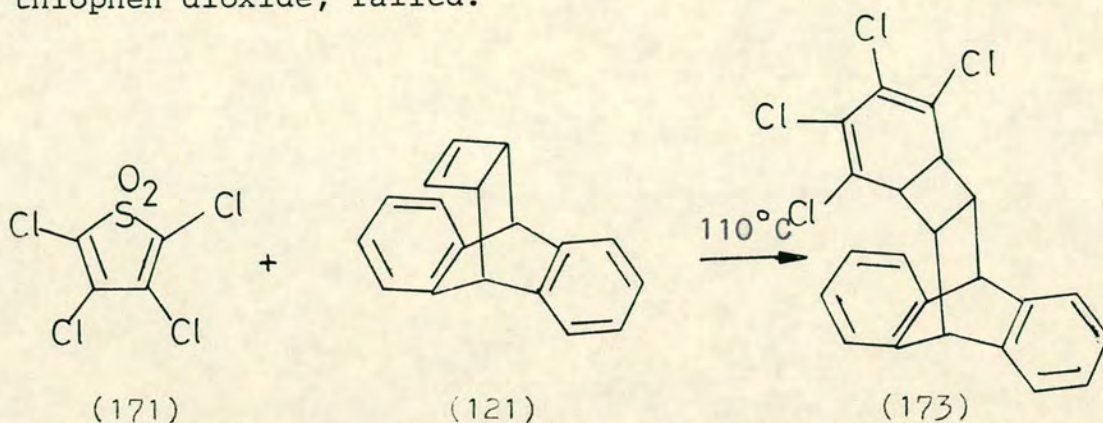
loss of CO and gave an almost quantitative yield of anthracene and 1,2,3,4-tetraphenylbenzene, both of which could be obtained by pyrolysis of (169) directly at the higher temperature.



Raasch¹³¹ has shown that tetrachlorothiophen-1,1-dioxide (171) readily undergoes Diels-Alder cycloaddition reactions with a wide variety of electron rich and electron poor alkenes. In a typical example, the cycloaddition with ethylene proceeded with loss of sulphur dioxide to give the product (172) in 89% yield.

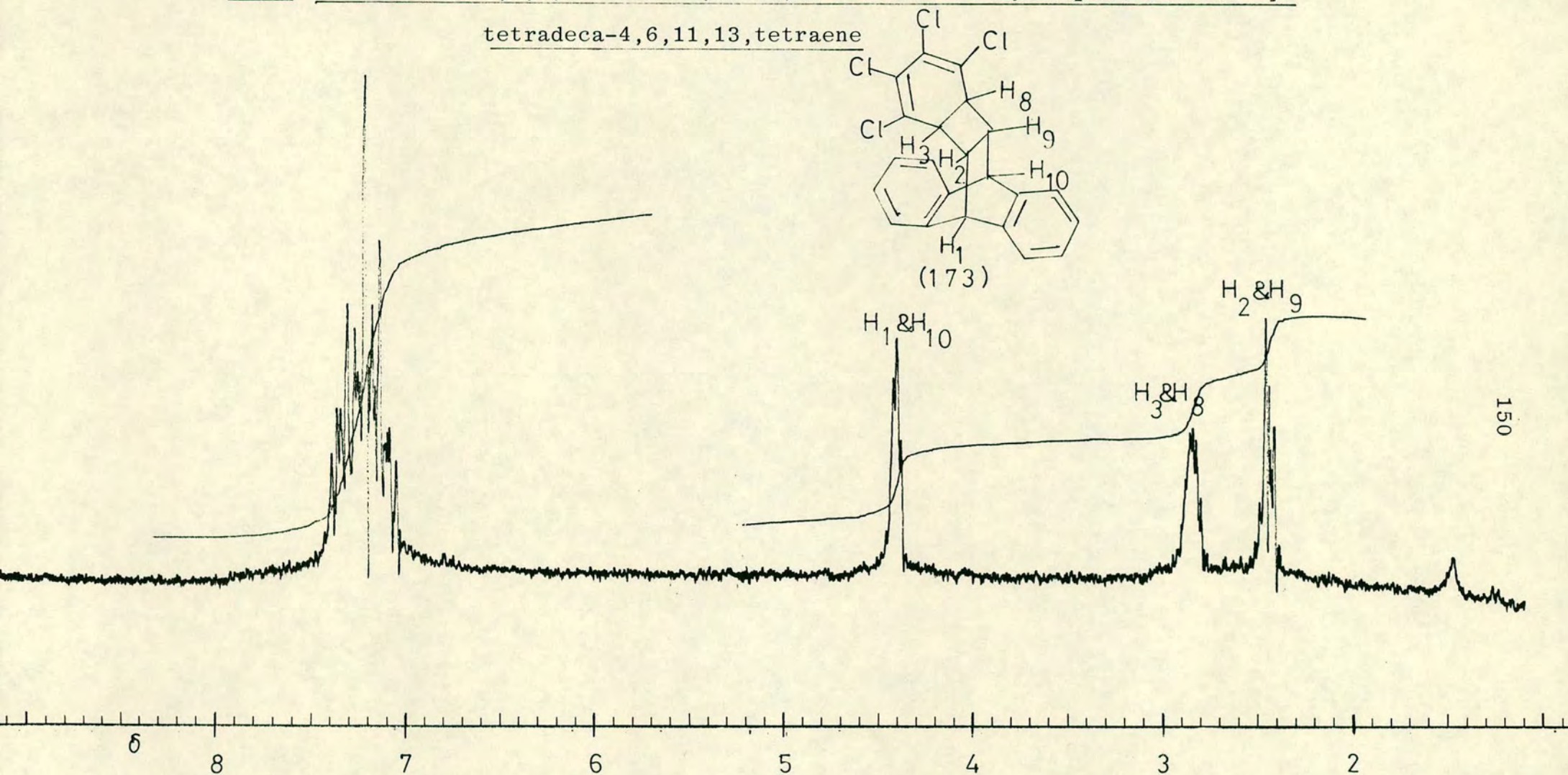


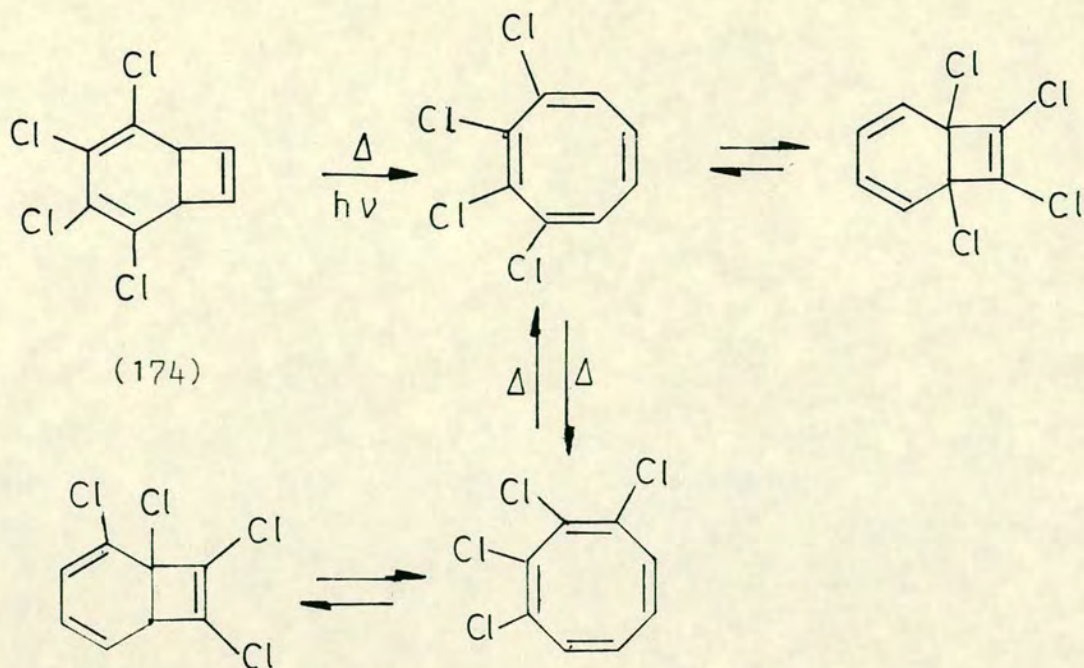
A similar reaction occurred with cyclobutananthracene (121) in boiling benzene to give the expected adduct (173) in 67% yield. An attempt to prepare the corresponding non-chlorinated adduct by reaction of the alkene (121) with thiophen dioxide, failed.



When the adduct (173) was subjected to F.V.P. at 600°C, decomposition occurred to give a mixture of three products as evidenced by g.l.c. analysis. Because of the presence of anthracene it was initially thought that 2,3,4,5-tetrachloro-bicyclo[4.2.0]octa-2,4,7-triene (174) may have been formed, but none of the expected peaks were observed in the ¹H-n.m.r. spectrum of the crude pyrolysate. Warrener *et al.*¹³⁴ have shown that the triene (174) undergoes a thermal rearrangement as shown in Scheme 41, but no n.m.r. evidence could be found for the presence of its thermal isomer in the pyrolysate.

Fig.8 ^1H -n.m.r. of 4,5,6,7-tetra-11,12:13,14-dibenzotetracyclo [8.2.2.0^{2,9}.0^{3,8}]-
tetradeca-4,6,11,13,tetraene

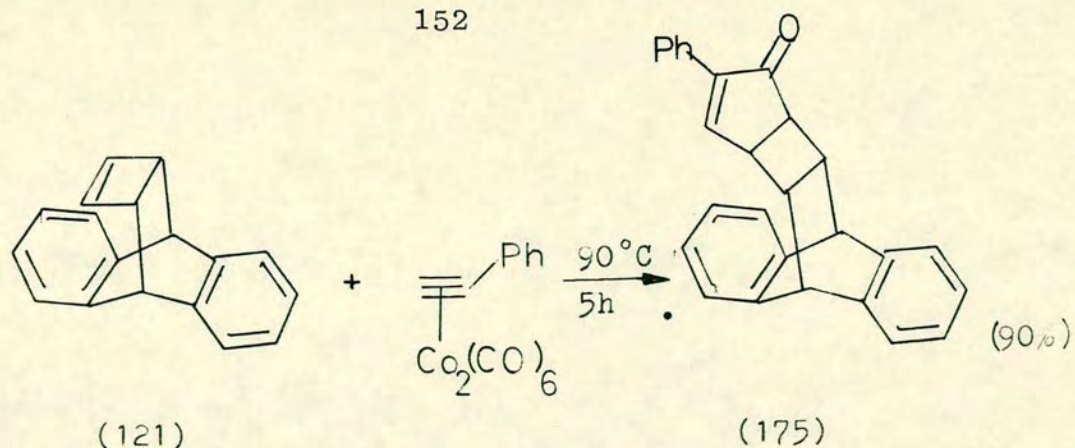




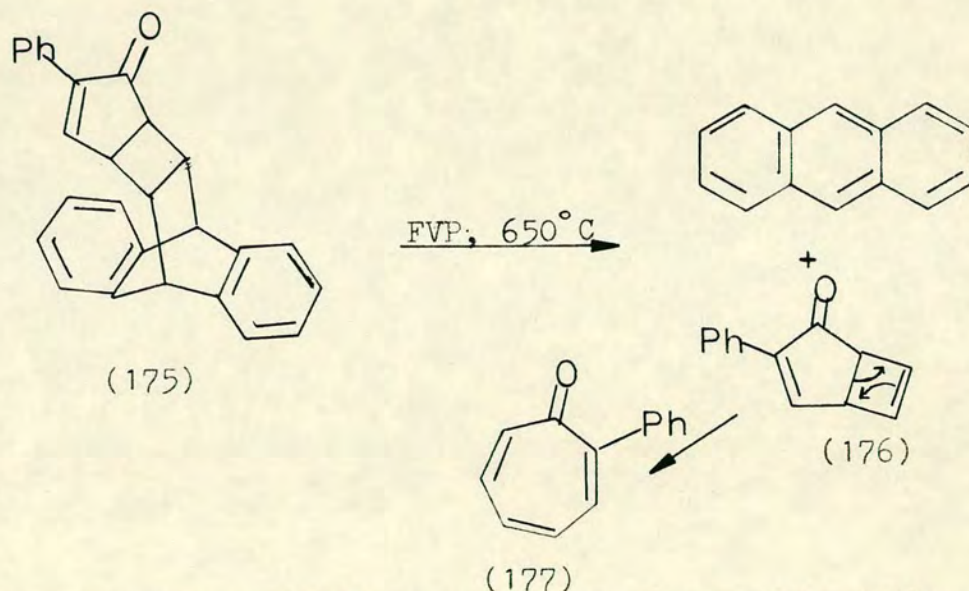
Scheme 41

By recourse to g.l.c.-mass spectroscopy and comparison with authentic samples, the pyrolysate mixture was identified as a mixture containing anthracene (36%), dibenzobarrelene (14%), and 1,2,3,4-tetrachlorobenzene (50%) - yields were based on ^1H -n.m.r. integrals. From the nature of these products it was clear that the adduct (174) had followed a different fragmentation pathway, preferring instead, to cleave the cyclobutane ring rather than eliminate anthracene directly. That (121) prefers to act as an acetylene synthon in this instance, as opposed to a cyclobutadiene synthon, is presumably a reflection of relative aromaticity of tetrachlorobenzene viz ~~vs~~ anthracene.

In a collaborative study with Dr. D.C. Billington of Strathclyde University, the ketone (175) was prepared in 90% yield by the method shown in Scheme 42.

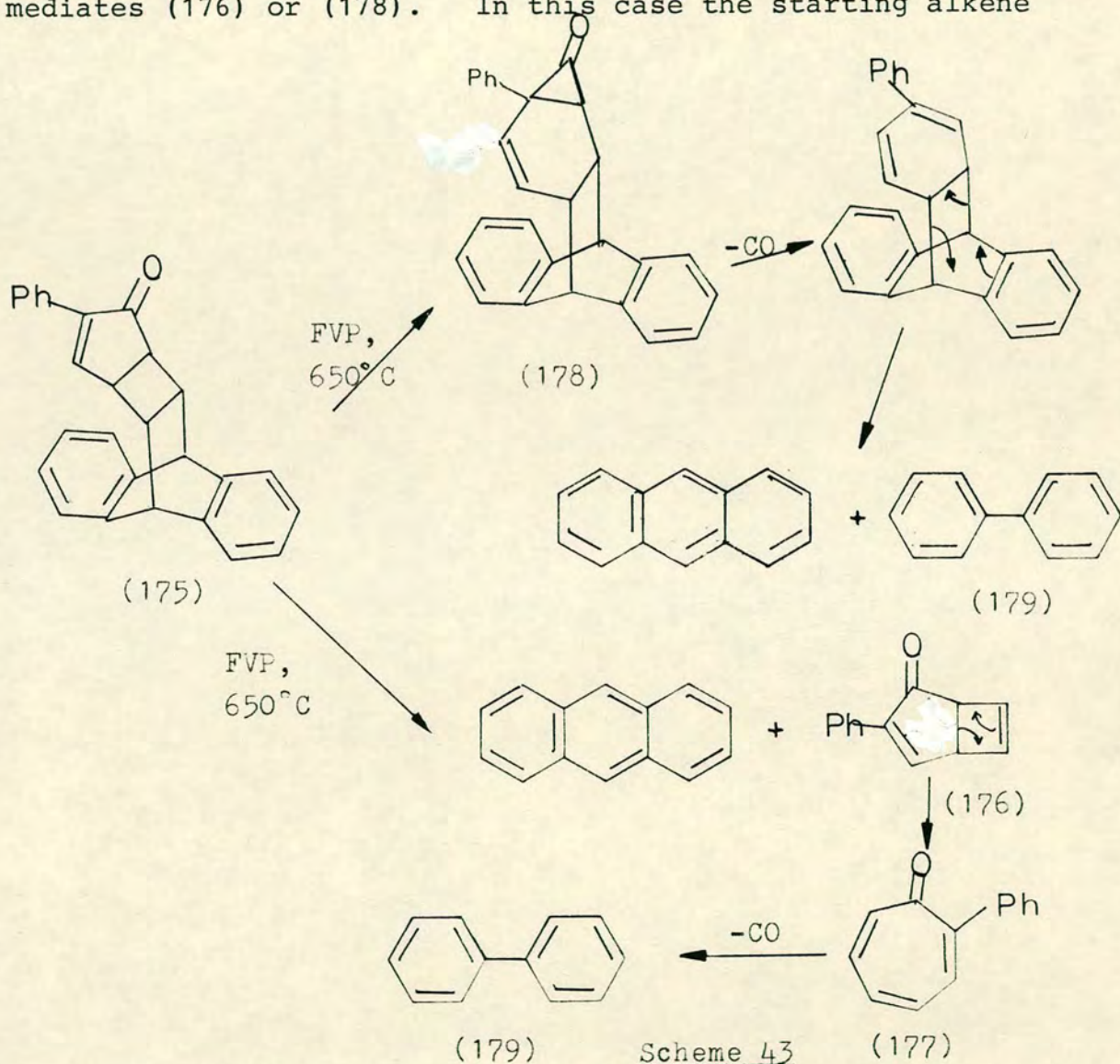
Scheme 42

It was envisaged that thermal fragmentation of (175) might lead to loss of anthracene and the formation of 2-phenyltropone (177) via (176). In the event F.V.P. of



the ketone (175) at 650°C gave a colourless solid (34%) whose ^1H -n.m.r. spectrum showed the presence of only aromatic protons, some of which were indicative of anthracene. T.l.c. provided evidence for the formation of two distinct compounds - an observation that was confirmed by g.l.c. analysis. Comparison with an authentic sample showed that one of the components was indeed anthracene. From g.l.c.-m.s. analysis, the other component was found to have a base peak at m/z 154. This information, coupled with the ^1H -n.m.r. spectral evidence of

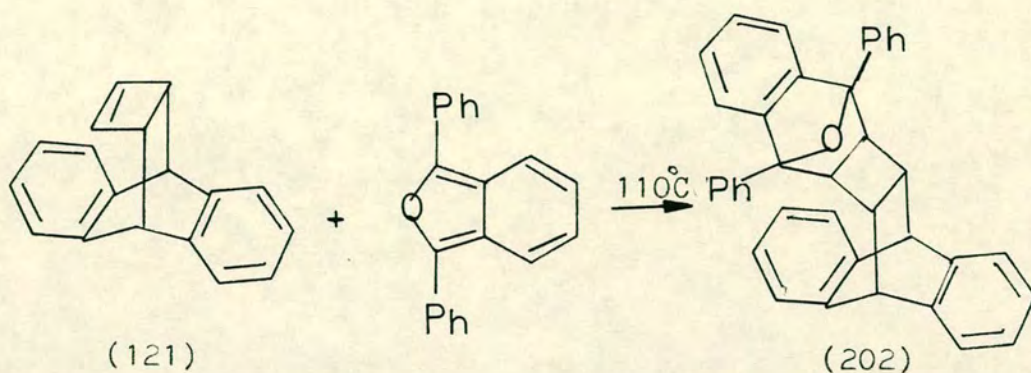
only aromatic protons, indicated the other compound to be biphenyl (179), which was subsequently proven by gl.c. by comparison with an authentic sample. The formation of (179) is unexpected, but can be rationalised by the mechanisms outlined in Scheme 43 whereby CO is eliminated from the intermediates (176) or (178). In this case the starting alkene



(175) functioned as a cyclobutadiene synthon in both possible pathways.

Cyclobutananthracene reacted with 1,3-diphenylisobenzofuran to give the adduct (202) in 53% yield as colourless crystals. Details of the pyrolyses products from this compound are

discussed collectively in Section C.4.

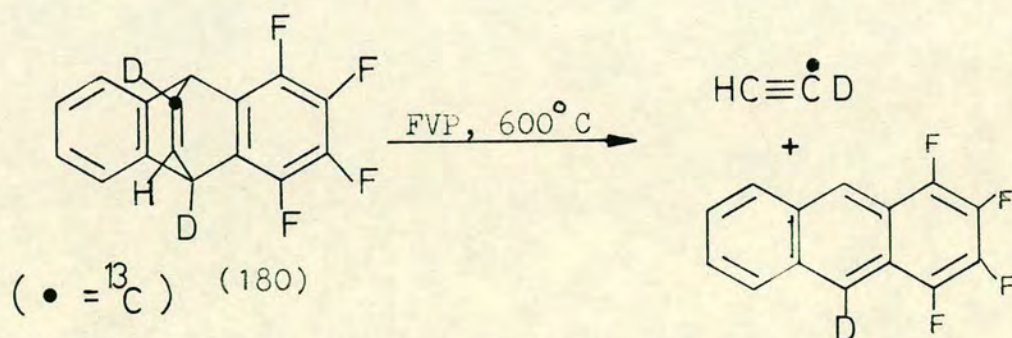


It should be observed that, in two of the adducts (160) and (175), cyclobutanthalracene acted as a cyclobutadiene synthon when pyrolysed. However, when the other adducts (161), (166), (169) and (173) underwent pyrolysis, the cyclobutanthalracene acted as an acetylene synthon, which implied the cleavage of dibenzobarrelene from the adduct. The products from these pyrolyses showed that the dibenzobarrelene could then decompose to give anthracene and presumably acetylene, although no acetylene was detected. This behaviour led to the further investigation of dibenzobarrelene as an acetylene synthon.

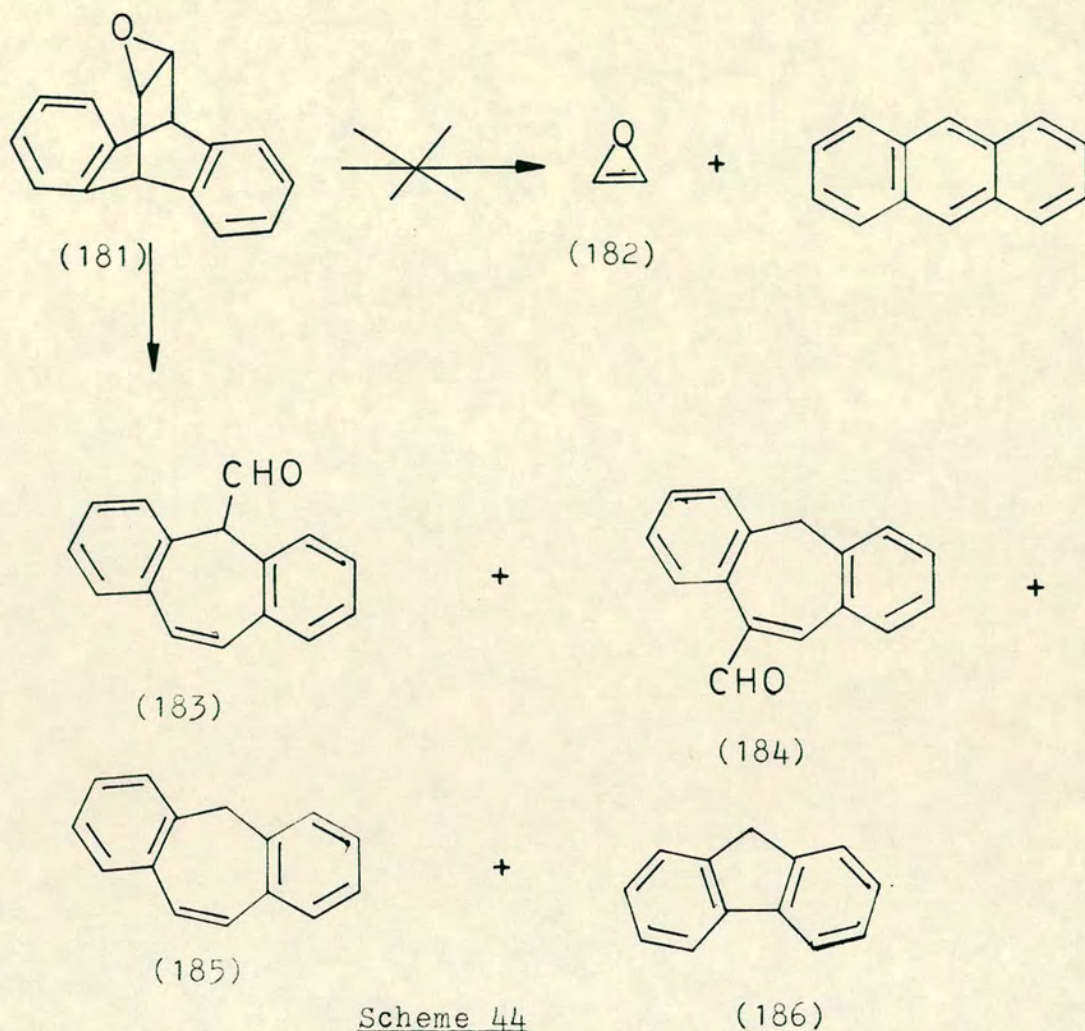
C. 5,6:7,8-Dibenzobicyclo[2.2.2]octa²₅,7-triene as an Acetylene Synth

1. Background

The observation of 5,6:7,8-dibenzobicyclo[2.2.2]octa-5,7-diene, hitherto known as dibenzobarrelene (37), in the products from the F.V.P. of adducts derived from 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (121) (p.144) was surprising. Its partial decomposition under these conditions to give anthracene and acetylene prompted an investigation into its possible use as an acetylene synthon. Prior to these studies, other related work that had been reported was by Brown et al.¹³⁵ who pyrolysed the substituted dibenzobarrelene (180) at 600°C to give a doubly-labelled acetylene.

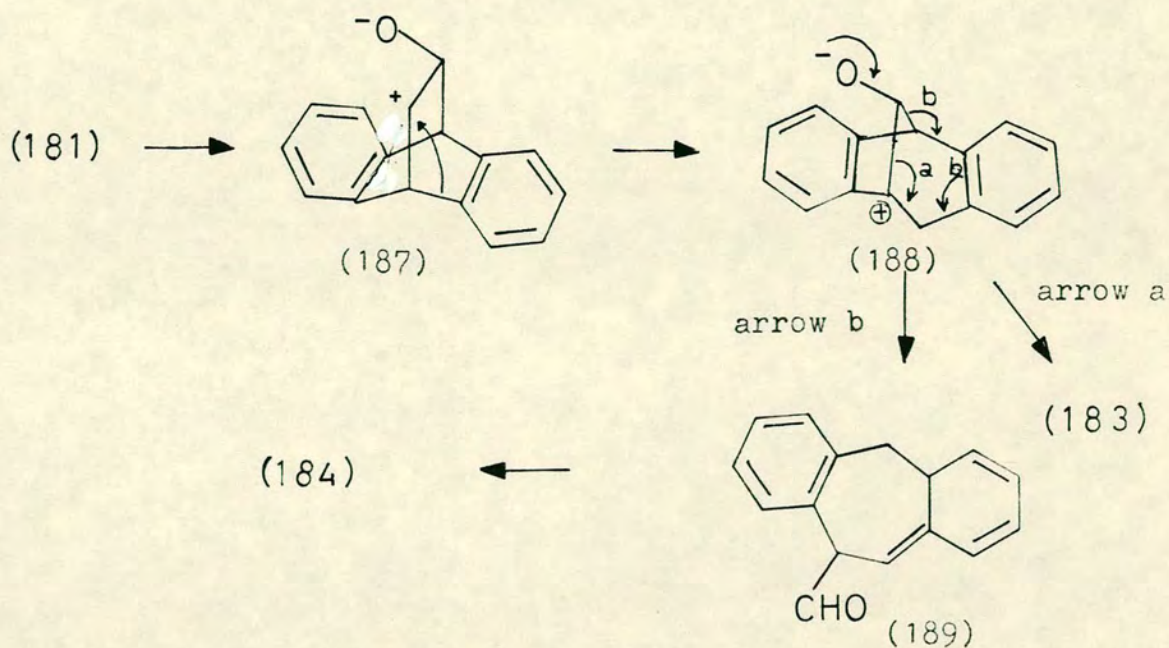


Lewars and Morrison¹³⁶ also examined the epoxide (181) as a potential precursor to oxirene (182). However pyrolysis of (181) at temperatures between 400-800°C did not proceed as expected but gave instead, depending on the temperature of the furnace, a mixture of (183), (184), (185), (186) and other unidentified compounds. The formation of (183) was rationalised by cleavage of the epoxide to (187) which undergoes a



Scheme 44

Wagner-Meerwein shift to form (188) followed by carbon-carbon bond cleavage (188 arrow a).¹³⁷ In an alternative reaction,



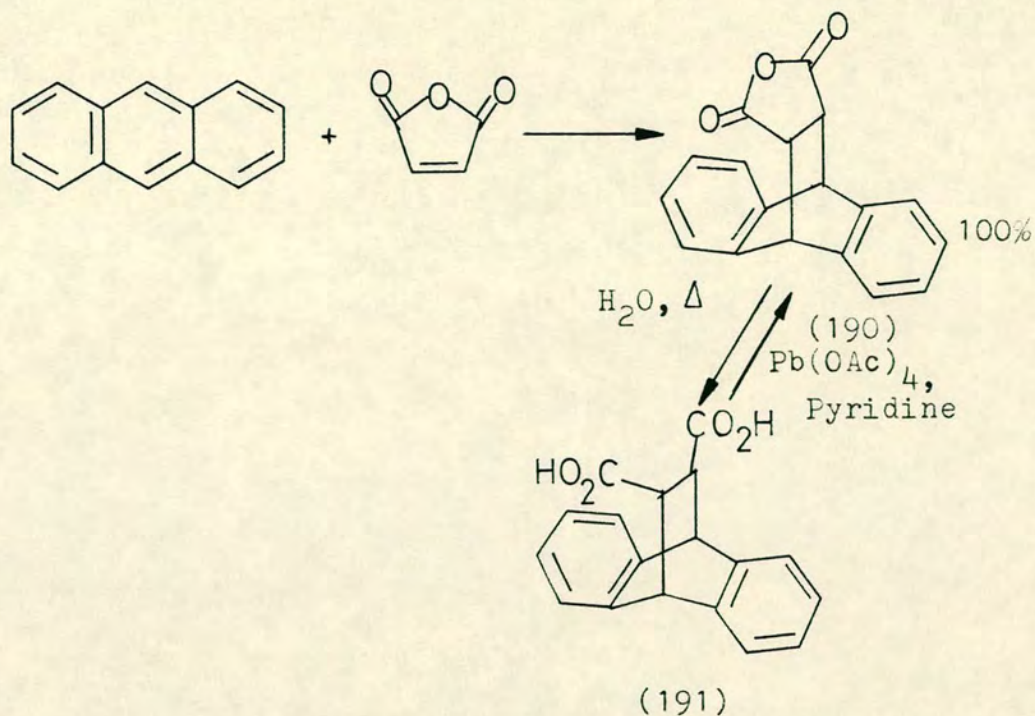
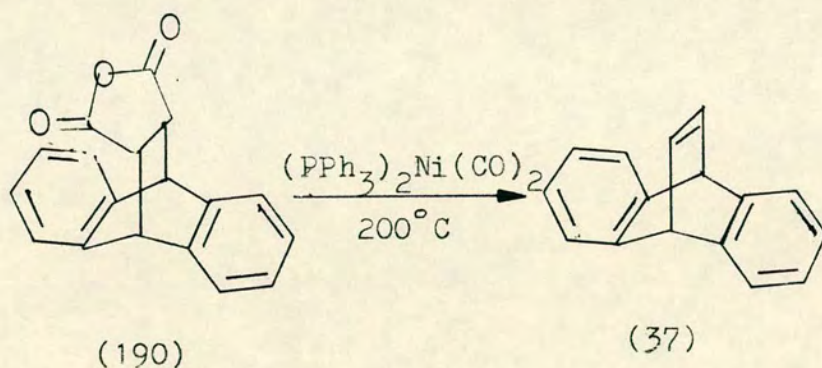
Scheme 45

cleavage of (188, arrow b) would give the o-xylylene (189) which could be converted into (184) by a 1,5-sigmatropic suprafacial shift of a hydrogen atom.

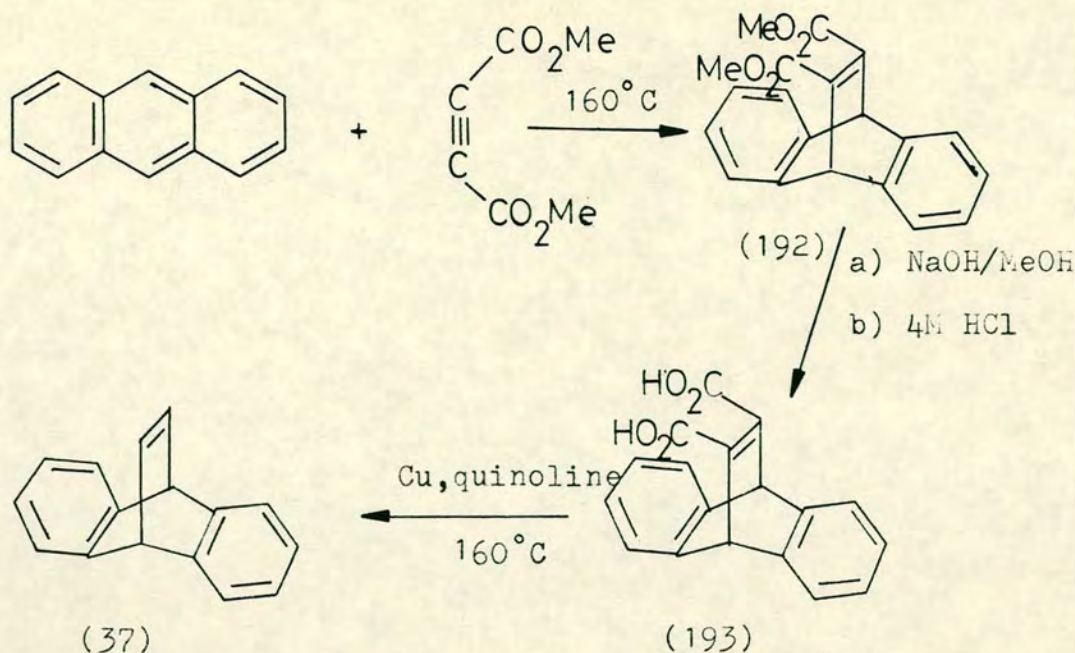
Despite the lack of success in the attempted synthesis of oxirene it seemed likely, from F.V.P. results with cyclobutanthracene adducts, that dibenzobarrelene was a potential acetylene synthon.

2. Preparation of 5,6:7,8-dibenzobicyclo[2.2.2]octa²-5,7-triene

In this work, initial attempts to synthesise dibenzobarrelene (37) met with varying degrees of success. The first approach, outlined in Scheme 46, involved a cycloaddition reaction with maleic anhydride followed by conversion of the expected adduct (190) into its diacid and subsequent oxidative decarboxylation. The first two steps proved successful, reacting in yields of 100% and 66% respectively, but the attempts to oxidatively decarboxylate the diacid (191) resulted in reversion to its anhydride, as discussed on p.135. In order to circumvent this problem the anhydride (190) was treated with bis(triphenylphosphine)nickel dicarbonyl in diglyme.²³ The procedure had proved successful in the synthesis of bicyclo[2.2.1]heptene²³ (see page 9) but gave only a 12% yield of dibenzobarrelene (37) from the diacid (191).

Scheme 46

The procedure finally adopted utilised the method of Figeys and Dralants,⁴ and involved the addition of anthracene to dimethyl acetylene dicarboxylate to give (192) in 76% yield, followed by the conversion of adduct (192) to the diacid (193) in 95% yield. When the diacid was heated under reflux in a copper-quinoline solution, decarboxylation occurred smoothly to give dibenzobarrelene, in 40% yield, as a colourless

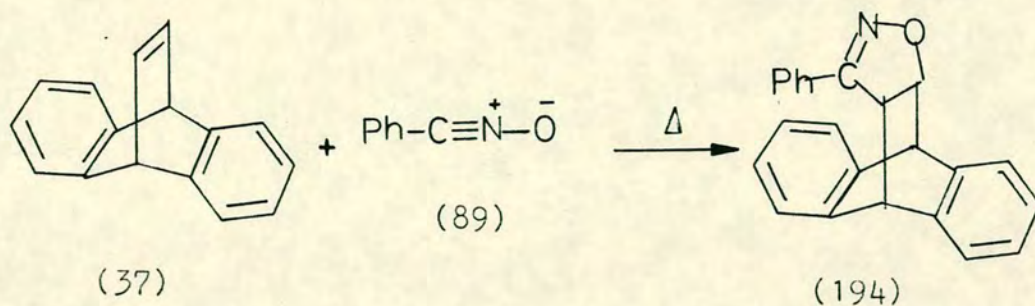


solid (mpt. $119-120^\circ\text{C}$; lit.⁷⁸ $119-120.5^\circ\text{C}$) with identical spectroscopic properties to those reported by Figeys and Dralants.

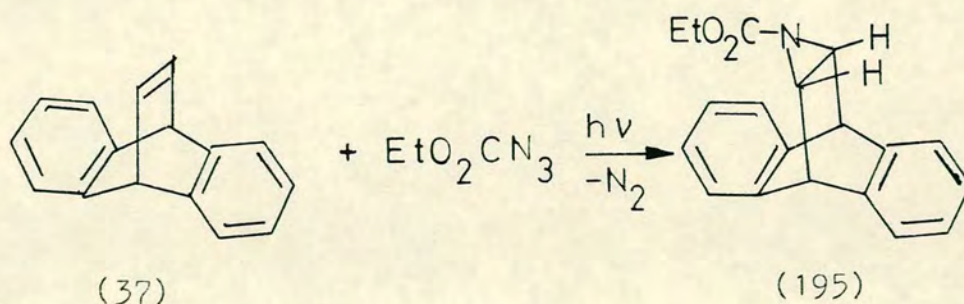
Under F.V.P. conditions dibenzobarrelene underwent ready fragmentation into anthracene and acetylene, but the extent of conversion depended upon the furnace temperature and the rate of sublimation. At 750°C with an inlet temperature of 80°C , conversion of 32% was achieved.

3. Cycloaddition reactions of 5,6:7,8-dibenzobicyclo-[2.2.2]octa-²5,7-triene

The reactivity of dibenzobarrelene towards 1,3-dipoles was found to be similar to that of cyclobutananthracene (121) and readily gave adducts in comparable yields. For example, reaction with benzonitrile oxide (89) in toluene at 20°C gave the adduct (194) in 64% yield. Under similar conditions



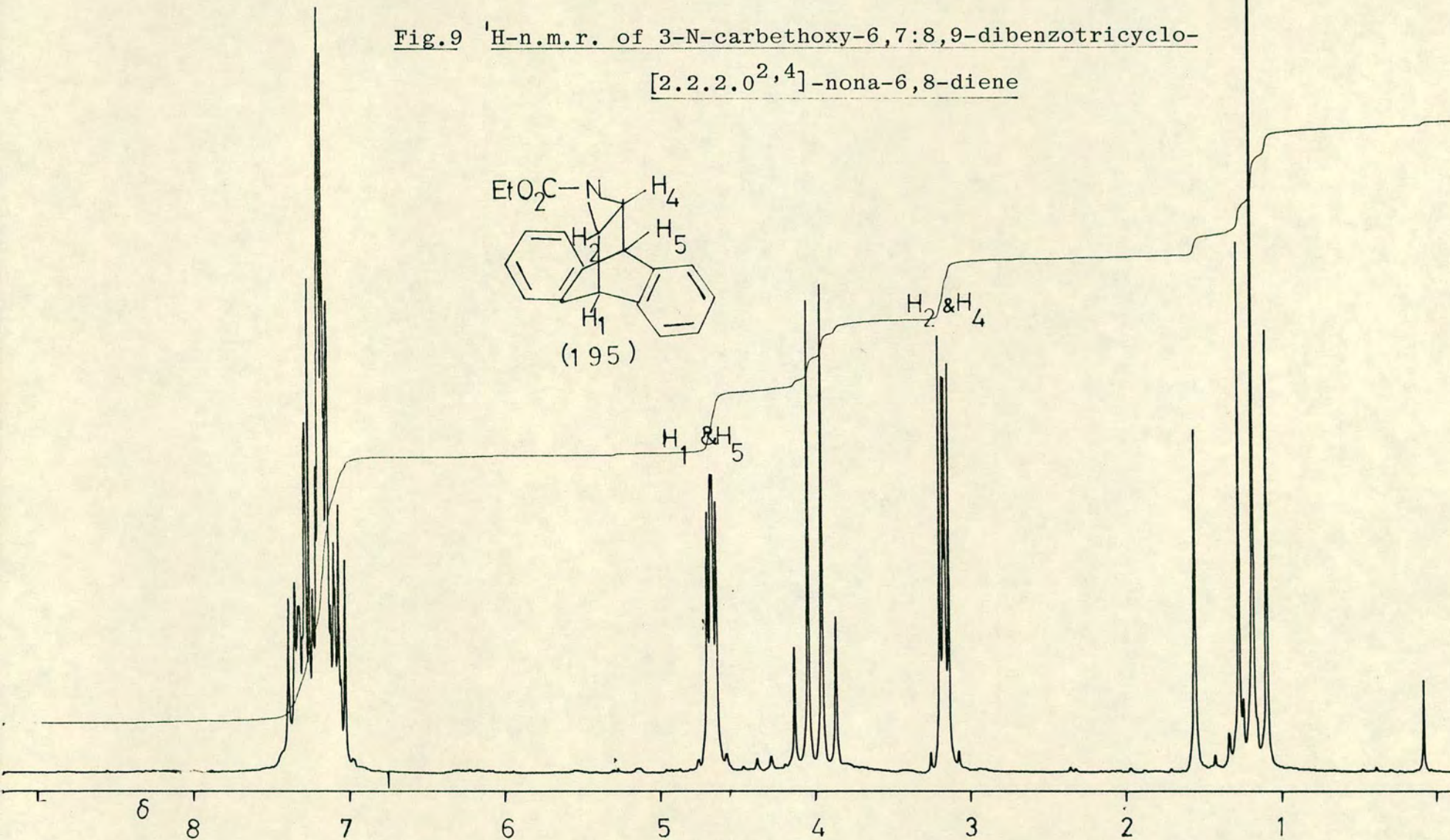
no reaction was observed with *p*-anisonitrile sulphide, the latter undergoing ready decomposition into the corresponding nitrile and sulphur. Dibenzobarrelene also reacted readily with ethyl azidoformate under photolytic conditions, a reaction that did not occur with cyclobutananthracene (121) [see p. 65], to give the adduct (195) in 39% yield as a colourless solid, mpt. 189–191°C. This corroborated fully with analytical and spectral results. It is not clear whether the mechanism for the formation of (195) involves a nitrene intermediate, or proceeds by way of cycloaddition via the electronically excited azide.¹³⁸ The structure proposed for (195) is consistent

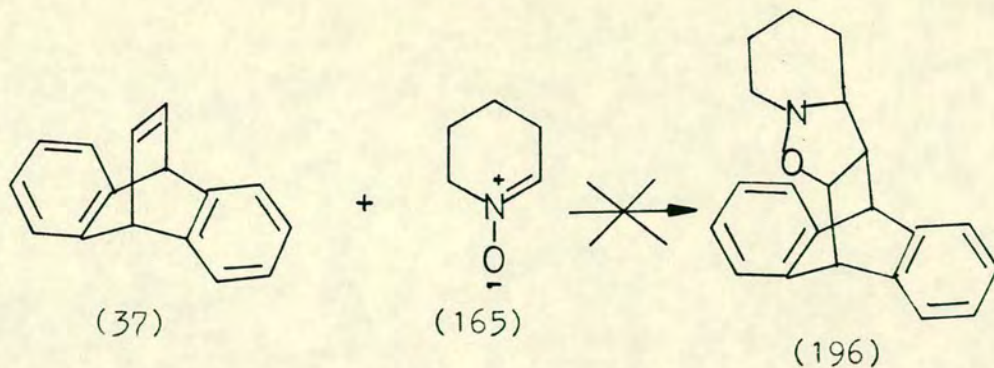


with its ¹H-n.m.r. spectrum which showed the presence of distinctive signals for the aziridine protons at 3.15 ppm.

In contrast to these reactions, that with 1-piperidine-^e_N-oxide (165) was unsuccessful giving rise to extensive

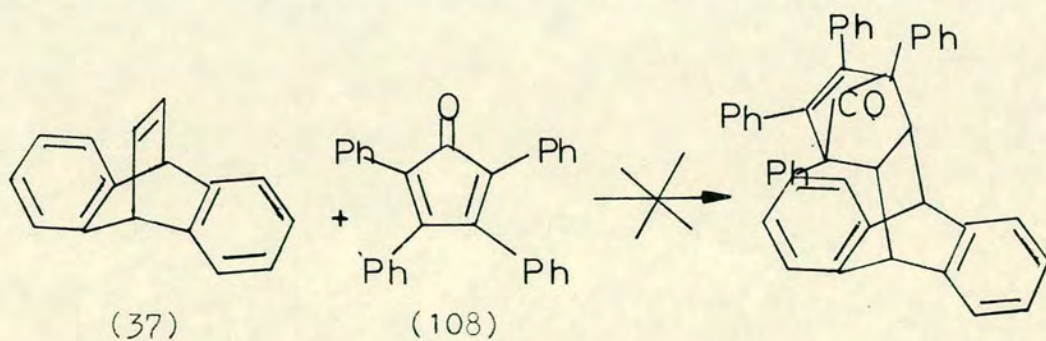
Fig.9 ^1H -n.m.r. of 3-N-carbethoxy-6,7:8,9-dibenzotricyclo-
[2.2.2.0^{2,4}]-nona-6,8-diene



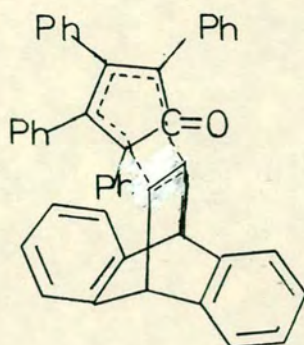


decomposition of starting materials. Bearing in mind the ease of decomposition of the corresponding adduct (166) from cyclobutananthracene, formation of (196) may well have occurred, followed by decomposition of the adduct under the reaction conditions required for cycloaddition.

Some difficulties were also experienced in attempts to prepare Diels-Alder cycloadducts with dibenzobarrelelene. In contrast to cyclobutananthracene it failed to react with tetracyclone (108) even in boiling xylene. This lack of



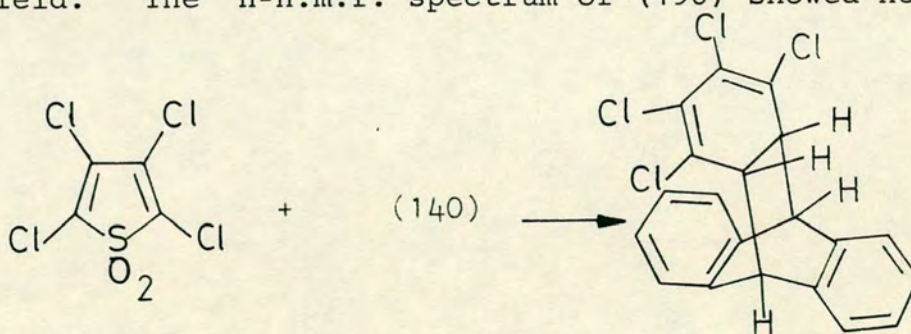
reaction was surprising given the similarity in their reactivity towards benzonitrile oxide. It may be a consequence of steric hindrance in the transition state (197), between the phenyl substituents of the tetracyclone and the benzo-groups of dibenzobarrelelene, that prevents reaction.



(197)

In the case of cyclobutananthracene, the double bond is one carbon atom further removed and this presumably relieves any strain arising from this interaction.

The corresponding reaction of dibenzobarrelelene with 2,3,4,5-tetrachlorothiophen-1,1-dioxide was more successful and gave rise to the product (198) by loss of SO_2 in 63% yield. The ^1H -n.m.r. spectrum of (198) showed none of the

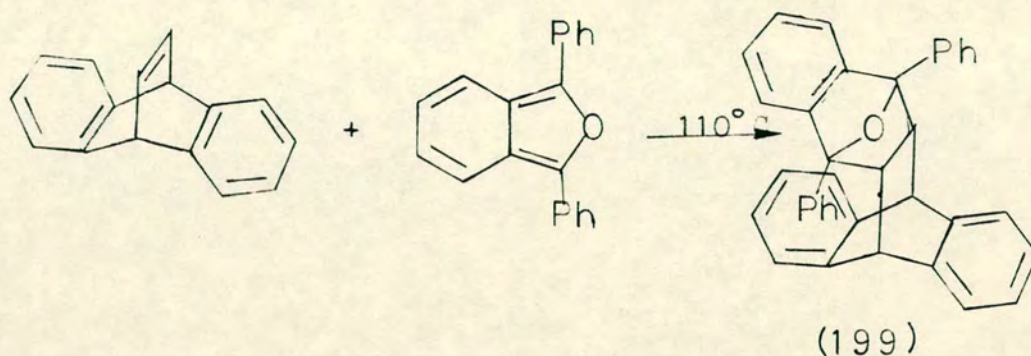


(198)

expected coupling between the H_1 and H_2 and the H_7 as seen, for example, with (173) (p.150). This is presumably due to the orthogonal nature of the carbon-hydrogen bonds involved¹³⁹ in the molecule.

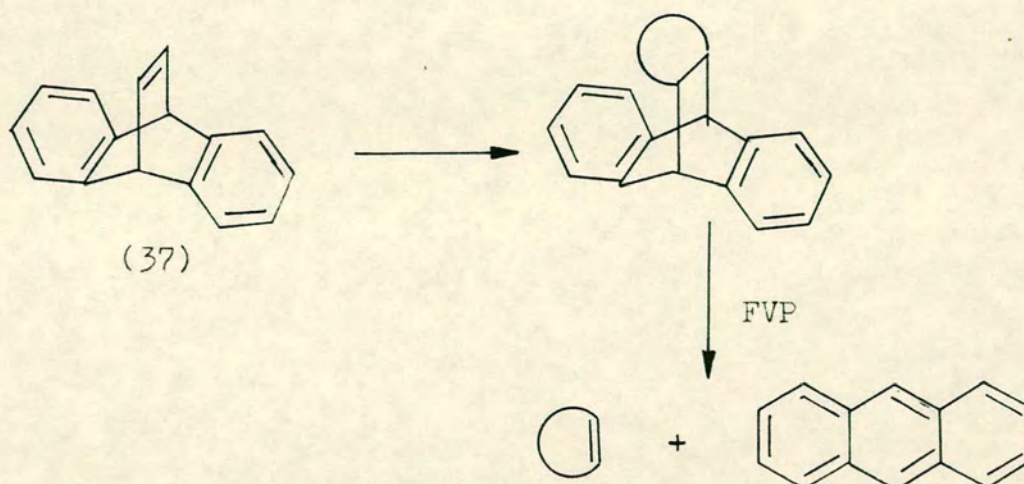
Lastly, in the case of 1,3-diphenylisobenzofuran, reaction with dibenzobarrelelene occurred in boiling toluene to give an adduct in 67% yield. This compound was identified as (199) on the basis of analytical, mass-spectrum and spectroscopic

data. In particular, it is worth noting that the bridge-head protons coupled although due to the broadness of the peaks an accurate coupling constant could not be calculated but it is estimated to be in the region of 1-3Hz.



4. Flash vacuum pyrolysis of cycloadducts derived from 5,6:7,8-dibenzobicyclo[2.2.2]octa-2,5,7-triene

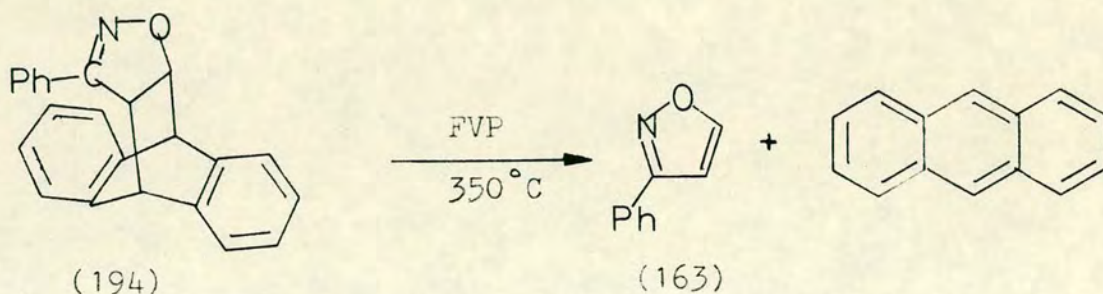
It was envisaged that pyrolysis of the title adducts would lead to fragmentation by loss of anthracene, thereby transferring an acetylene moiety to the cycloaddend (Scheme 47).



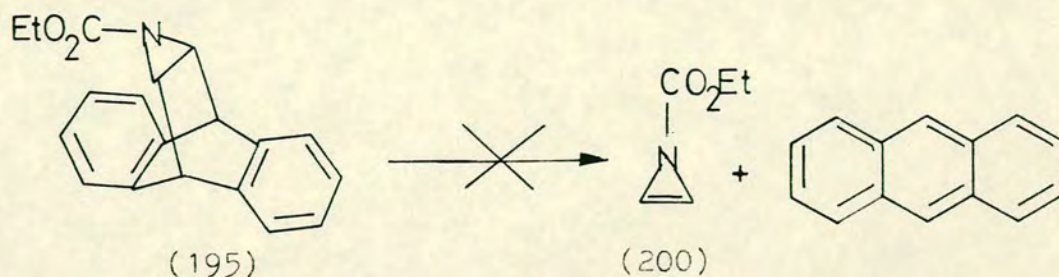
Scheme 47

As stated at the beginning of this chapter, this approach was adopted in the case of the epoxide (181) in the hope of producing oxirene itself, but failed, apparently because of the occurrence of an energetically more favourable ring-expansion.

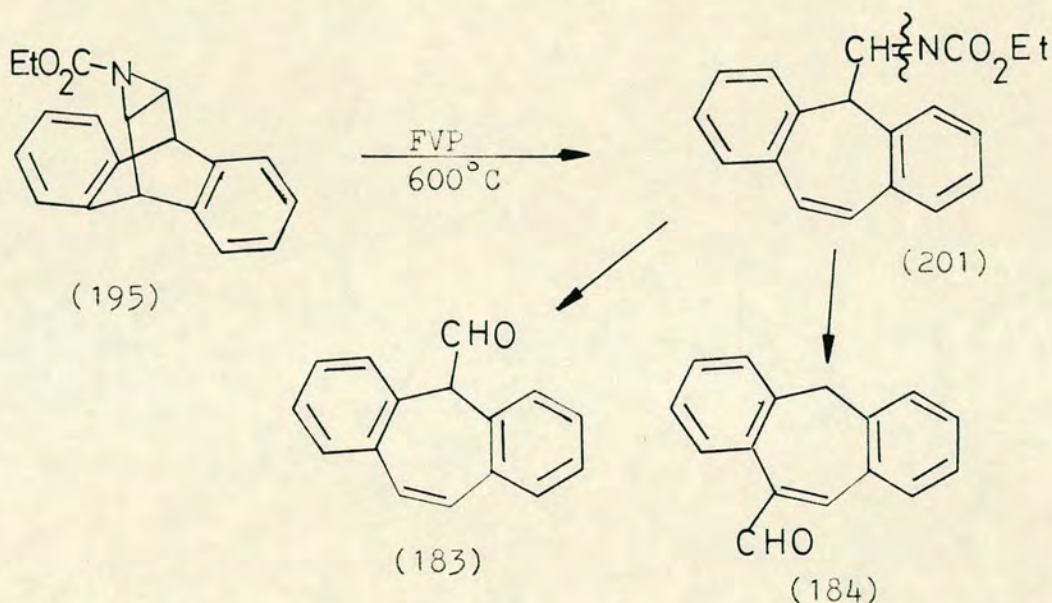
In the case of (194) F.V.P. at 350°C caused cleavage of the molecule to give 3-phenylisoxazole (163) and anthracene in a yield of 80% and 50% respectively with no other products, as evidenced by ^1H -n.m.r. spectroscopy. The ^1H -n.m.r. spectrum of the 3-phenylisoxazole was identical to that reported.⁷¹



When the corresponding aziridine (195) was subjected to F.V.P. it was expected that the 2-azirine (200) might be formed by a similar retro-cleavage. However such compounds are considered to be anti-aromatic owing to their 4π electron nature¹⁴¹ and, unlike the corresponding 1-azirines, have hitherto remained undetected.



Indeed F.V.P. of the aziridine (195) over a range of temperatures gave no immediately identifiable products other than anthracene, although preparative t.l.c. of the crude reaction mixture did give an apparently pure compound whose ^1H -n.m.r. spectrum contained an aldehydic proton at $\delta 9.98$. Its mass spectrum showed a parent peak at m/z 220 corresponding to $\text{C}_{16}\text{H}_{12}\text{O}$. This compound corresponded to either of the aldehydes (183) or (184), both of which had been obtained from the pyrolysis of epoxide (181) (see p.156).

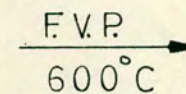
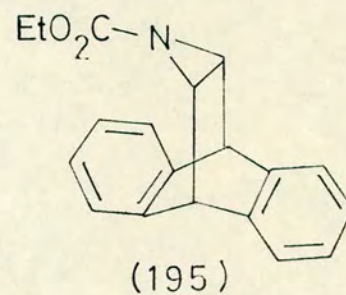


In order to explain the formation of this unexpected product, it seems likely that the aziridine (195) undergoes a similar thermal rearrangement to form the imine (201), which is then hydrolysed during work up on the preparative plate as outlined in Scheme 48.

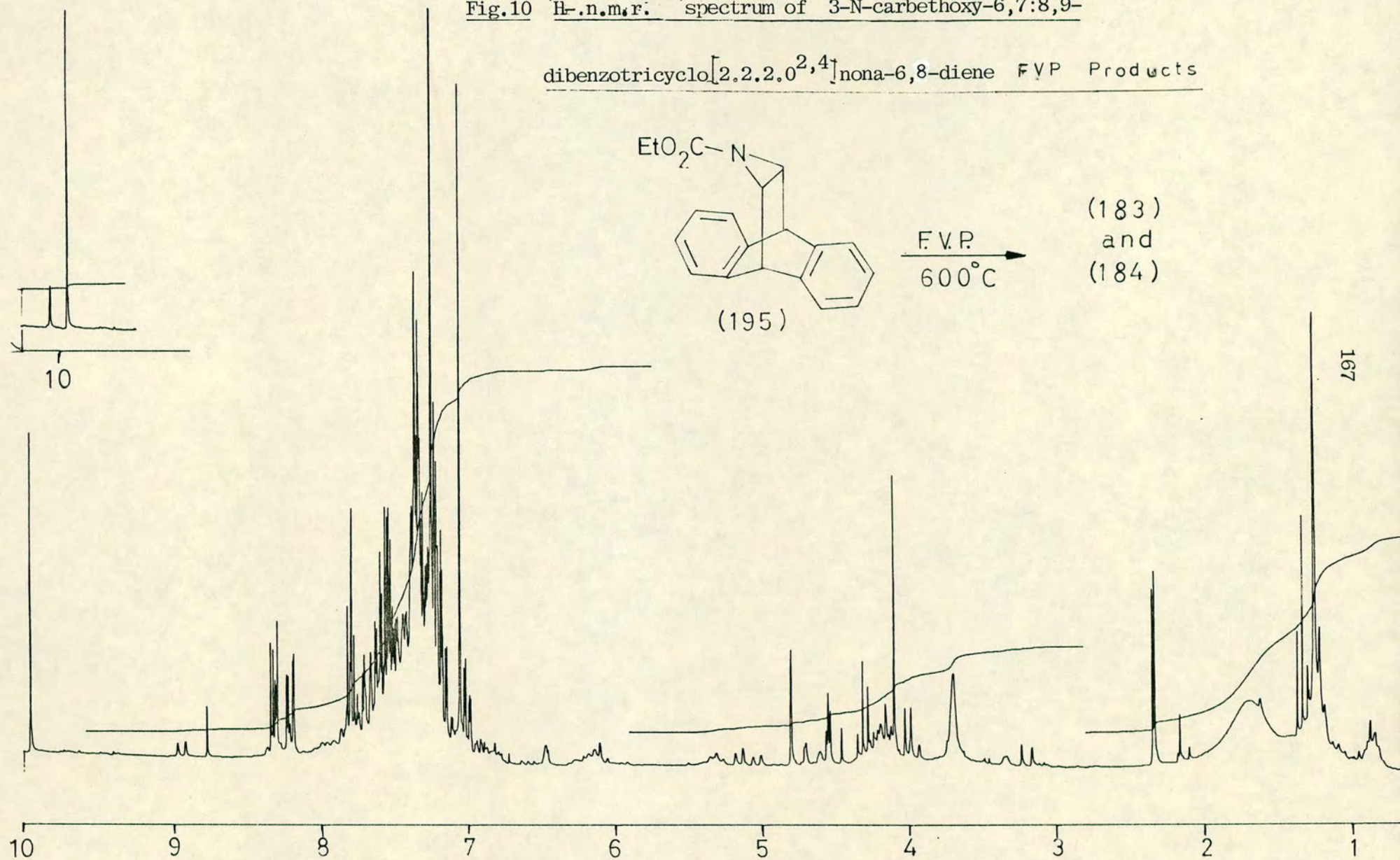
Pyrolysis of the adduct (198), which was formed from the reaction of dibenzobarrelelene with 2,3,4,5-tetrachlorothiophen-1,1-dioxide, at 580°C gave anthracene and tetrachlorobenzene

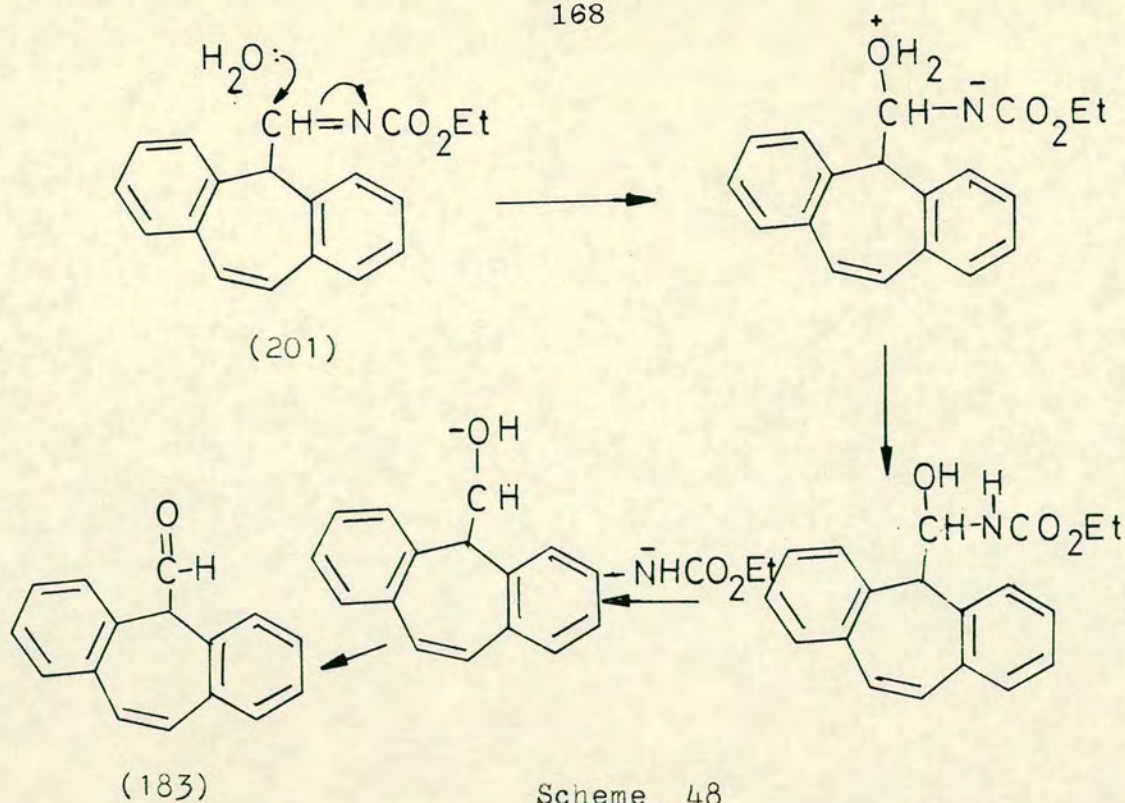
Fig.10 ^1H -n.m.r. spectrum of 3-N-carbethoxy-6,7:8,9-

dibenzotricyclo[2.2.2.0^{2,4}]nona-6,8-diene FVP Products

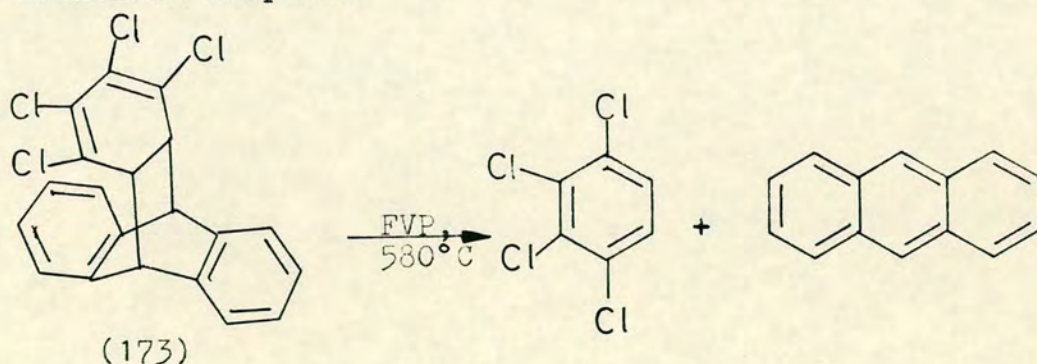


(183)
and
(184)

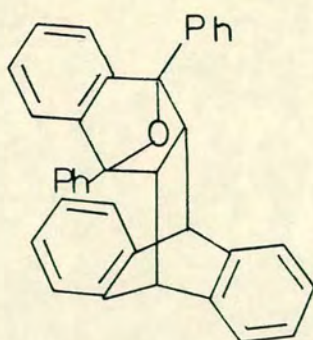




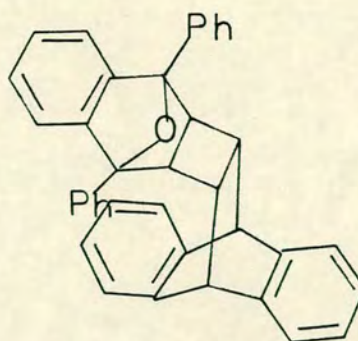
as the only products in yields of 91% and 94%, respectively. Confirmation of both products was given by g.l.c. comparison with authentic samples.



The F.V.P. of compound (199) gave a colourless oil whose ^1H -n.m.r. spectrum showed it to contain only aromatic protons, and was identical to that obtained from the pyrolysis of compound (202), the adduct obtained from the corresponding reaction of 1,3-diphenylisobenzofuran with 7,8:9,10-dibenzo-tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (see p.154). In both cases, the initial product from the pyrolysis was a yellow oil

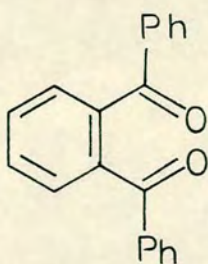


(199)



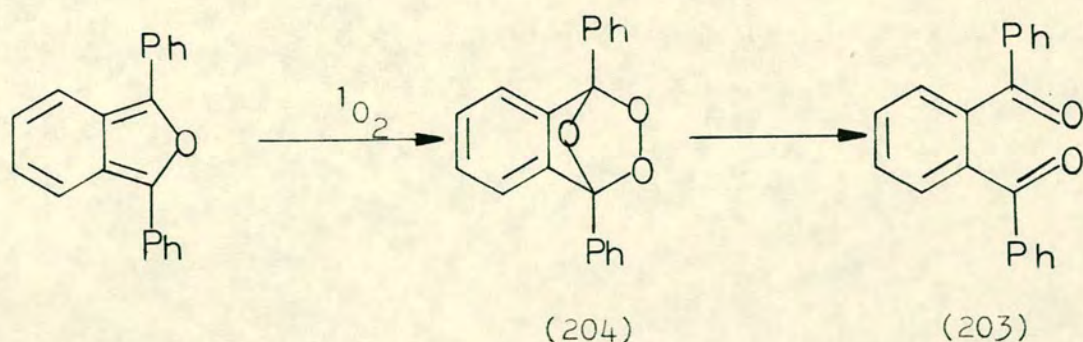
(202)

which gradually became colourless when left overnight. The i.r. spectrum of the oil showed an absorption at 1665 cm^{-1} indicating the presence of a carbonyl group. The mass spectrum showed a parent peak of m/z 302 and a peak at m/z 286. The ^1H -n.m.r. of this compound showed only aromatic protons to be present. However, F.V.P. of 1,3-diphenylisobenzofuran at 600°C showed no such compound to be formed, indeed showed it only to sublime under these F.V.P. conditions. On the evidence presented the structure would appear to be (203). This

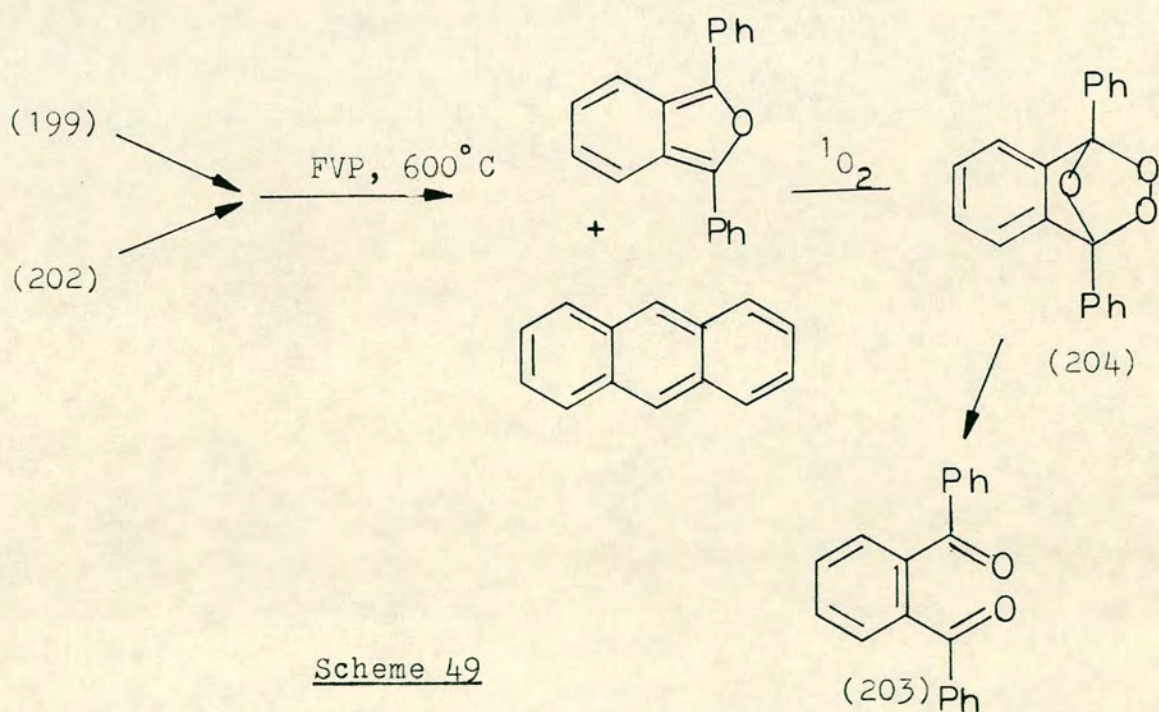


(203)

structure was corroborated by work done by several research workers^{142,143} who realised that benzo[c]furans were sensitive to oxygen, especially in the presence of sunlight, to give (203). Dufraisse and Ecary^{144,145} isolated the precursor of (203), the photooxide (204). As can be seen (203) and (204)

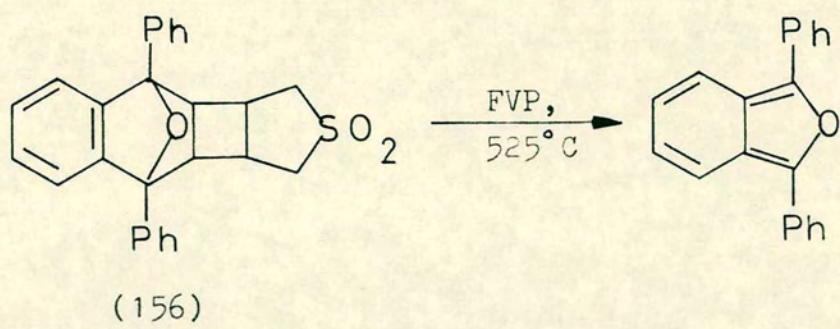


are responsible for the ion peaks m/z 302 and 286 respectively. Strangely, the 1,3-diphenylisobenzofuran extruded from (199) and (202) was not subjected to substantial photooxygenation. However, an explanation for this occurrence was provided by Adams and Wilkinson¹⁴⁶ who used anthracene as an efficient singlet oxygen photosensitiser. Thus, in the pyrolysis of (199) and (202) the mechanism is as Scheme 49.



Scheme 49

These reactions are contrasted with the F.V.P. of (156) which gave mainly 1,3-diphenylisobenzofuran at 525°C.

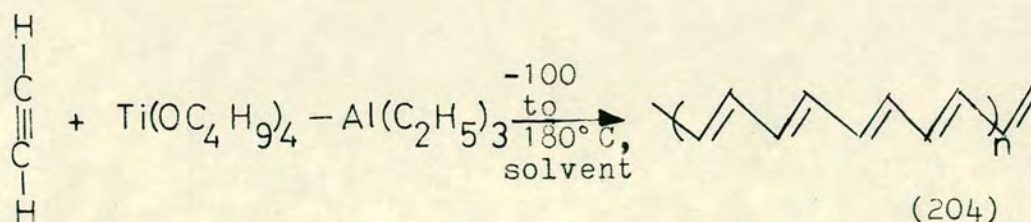


D. 7,8:9,10-Dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene
as a Precursor of Polyacetylene

1. General background

The current world-wide interest in electroactive polymers is focussed on electrically conducting and semiconducting polymers. These are an entirely new class of electrically active materials which offer new preparative routes, unconventional properties and thus, quite possibly, a wide range of novel potential applications. Of these polymers, polyacetylene (204) is the simplest polymer to display the semiconducting and conducting properties.

The first major synthesis of poly(acetylene) from acetylene was carried out by Shirakawa et al.¹⁴⁷ by passing acetylene over Ziegler type catalysts such as the $\text{Ti}(\text{OC}_4\text{H}_9)_4\text{-Al}(\text{C}_2\text{H}_5)_3$ system.



Throughout the 1960's several groups¹⁴⁸⁻¹⁵⁰ showed that poly(acetylene) was a semiconductor whose conductivity and thermal coefficient varied according to structural isomers, degree of crystallinity and exposure to oxygen. One group¹⁵⁰ showed that reaction with donor and acceptor gases markedly increased the electrical conductivity, and another group¹⁵¹

studied the effect of changing catalyst conditions on the structure and the electrical conductivity of the poly(acetylene) produced.

It was from the group studying catalyst conditions¹⁵¹ that a breakthrough came. They discovered that, if acetylene was passed over the surface of a 100-fold overconcentrated Ziegler Natta catalyst solution of titanium t-butoxide and triethylaluminium, then a thin, flexible film of poly(acetylene) was produced. It was shown that the structure of these films was, in fact, that of a tangled fibrillar mat. It was also cis- and trans-main chain double bonds. The trans-stereoisomer is the preferred type since it is more stable, and the cis-isomer can be converted to the trans-isomer by heating above 100°C.

In 1978 MacDairmid et al.¹⁵² doped poly(acetylene) with electron acceptors, such as iodine and arsenic pentafluoride, and with donors, such as sodium. This doping could increase the conductivity of the as-produced polymer by up to ten orders of magnitude through a semiconductor-metal transition to give conductivities of up to 10^3 Scm^{-1} .

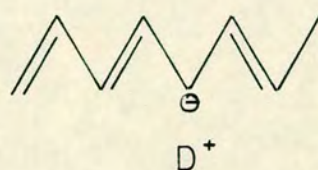
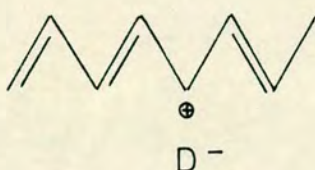
The conduction mechanism can be explained by two main conduction mechanisms known as the soliton and the percolation mechanisms.

The soliton mechanism relies on the rearrangement of electrons on the backbone. The soliton itself is an inversion of the π electron wave function and can be imagined as an interchanging of single and double bonds along a backbone. This inversion is thought to be spread over 12-16 double bonds and can be seen by electron spin resonance spectroscopy as a

free electron.



Doping destroys this free spin and induces charge



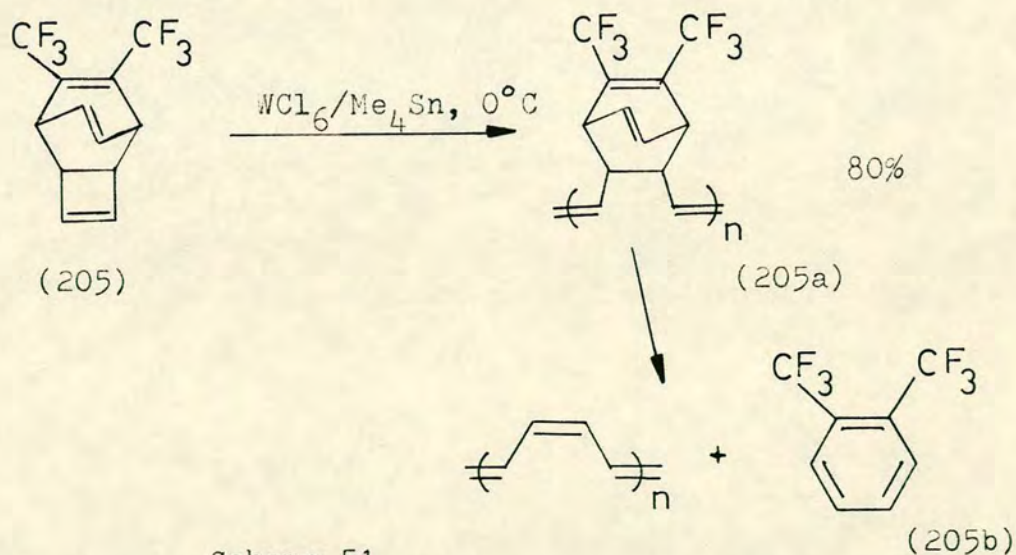
carriers which migrate along single chains within the fibril.

The percolation theory¹⁵³ argues that doping proceeds inhomogenously and produces random metallic-like droplets whose number increase until, at the semiconductor-metal transition, they form continuous paths through the material.

Whilst the percolation model is general enough to be applied to other conducting polymers, the soliton model is specific to poly(acetylene) chemical structure since it relies on degeneracy. Recent experiments have suggested that the effects which gave rise to the soliton theory can be found in other conducting polymers.

In view of the fact that poly(acetylene) quickly becomes inactive on exposure to air, the objective of more recent synthetic research has been the synthesis of a soluble, stable and well characterised polymer which could be converted into poly(acetylene) where and when required.

One such approach involves the metathesis of cyclobutene derivatives. In an elegant experiment, Feast and Edwards¹⁵⁴ used 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (209), formed from the thermal reaction of hexafluorobut-2-yne and cyclooctatetraene, as a precursor for the first synthesis of poly(acetylene) that permitted its formation as a workable thin film. When the monomer (205) was metathesised with tungsten hexachloride/tetramethyl tin catalyst in chlorobenzene, polymerisation occurred at the cyclobutene ring to give the soluble pre-polymer (205a) of \bar{M}_w 400,000. Subsequent decomposition of (205a) at 150-210°C under vacuum led to the elimination of 1,2-bis(trifluoromethyl)benzene and the generation of poly(acetylene) as a thin black film. However the



Scheme 51

extrusion of 1,2-bis(trifluoromethyl)benzene (205b) was found to be not entirely complete, probably because some of the relatively large aromatic molecules were trapped within the matrix of the poly(acetylene) as it was generated.

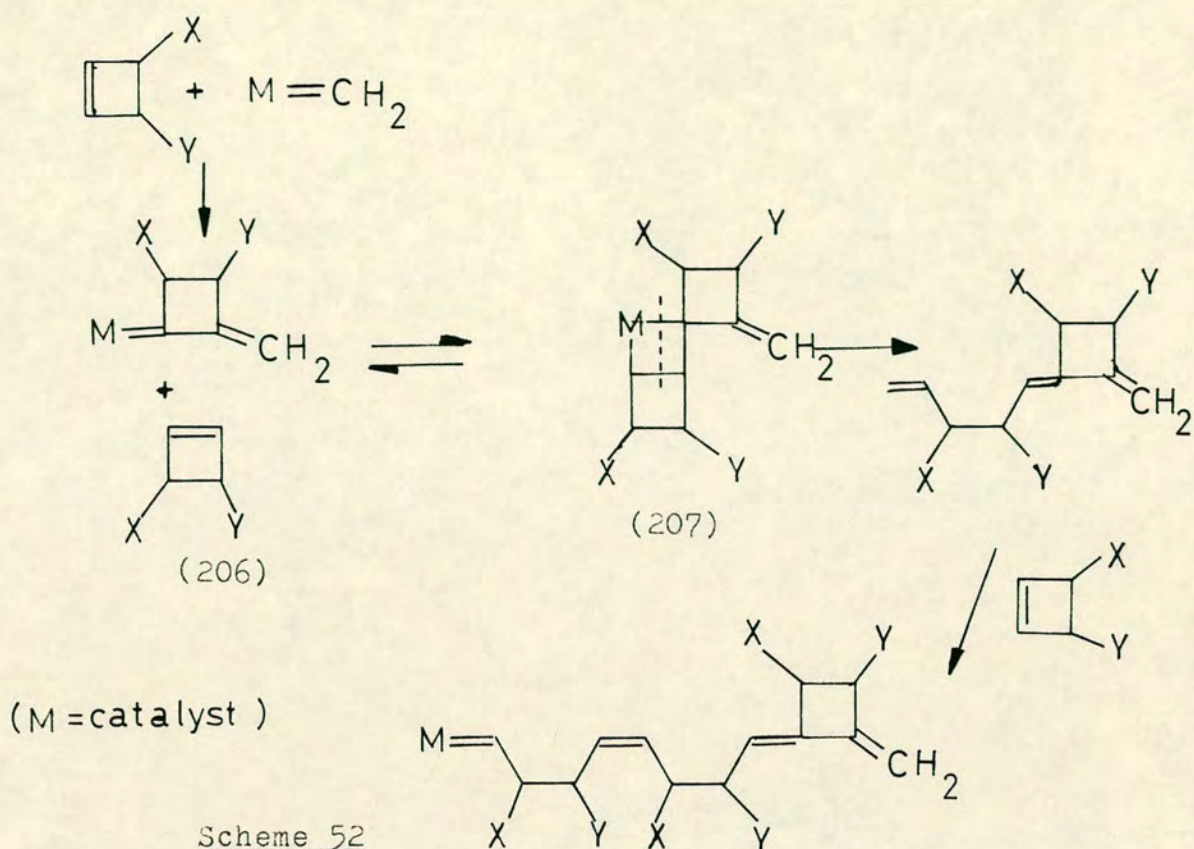
Other polymers can conduct electricity such as poly-(1,6-heptadiyne),¹⁵⁵ poly(p-phenylene), poly(p-phenylene

sulphide), poly(pyrrole)¹⁵⁶ and poly(thiophene) but none of these are as conductive as doped polyacetylene.

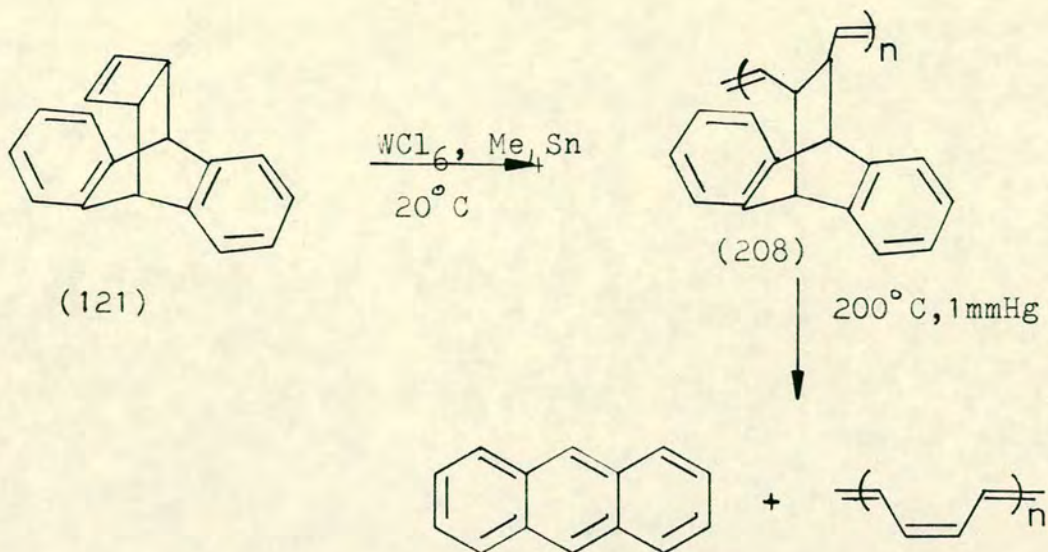
2. The novel synthesis of poly(acetylene) from 7,8:9,10-dibenzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene

It was recognised that cyclobutanthalracene (121), because of the strained cyclobutene ring, should also undergo metathesis. Moreover, thermolysis of the resulting polymer might lead to the formation of poly(acetylene) by loss of anthracene, a recognised leaving group in eliminations.

The metathesis reaction on cyclobutanthalracene (121) was performed using tungsten hexachloride/tetramethyltin as the catalyst system in chlorobenzene. This catalyst system, one of many, is perhaps the most widely used and was introduced by van Dam and co-workers¹⁵⁷ for the metathesis of long-chain fatty acid esters. It is now accepted that olefin metathesis under such conditions^{48,158} proceeds via a chain reaction, involving metal-carbenes that react reversibly with the olefin (206) via a metallacyclobutane intermediate eg. (207). The mechanism of reaction with a substituted cyclobutene is shown in Scheme 52.



Because the catalyst systems are extremely susceptible to poisoning and deteriorate on standing, norbornylene was used as a control to test the efficiency of the catalyst prior to its reaction with cyclobutananthracene (121). For these reactions it is essential to use dry and very pure reactants, as well as solvents, in a dry nitrogen atmosphere. Under the aforesaid conditions, cyclobutananthracene (121) readily underwent metathesis with $\text{WCl}_6/\text{Me}_4\text{Sn}$ to give poly-(cyclobutananthracene) (208), after 2 min reaction at 20°C , as a stable polymer at room temperature. The molecular weight of this polymer was given as \bar{M}_w 40,000 by G.P.C. analysis.



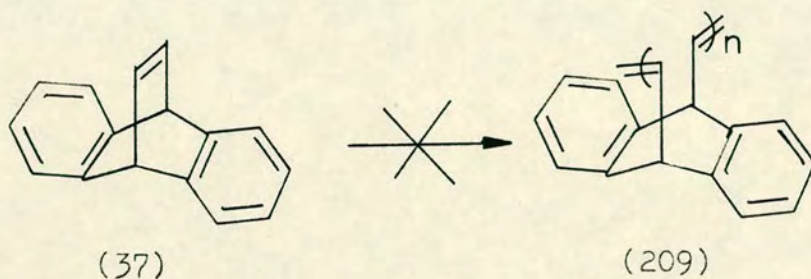
The polymer (208) could be spread as a thin film inside a glass tube and when it was subjected to conditions of $200^\circ\text{C}/1\text{ mmHg}$, anthracene in 42% yield was obtained on a cold finger. Higher temperatures did not produce more anthracene. The observation that not all the anthracene could be removed was subsequently confirmed by others.¹⁵⁹ The remaining polymer became orange after heating, this particular colour being indicative of an increase of conjugation within the polymer, and is recognised as a step leading to the formation of poly(acetylene).

It is thought that the problem of elimination of the anthracene from polymer (208) may be improved if a co-metathesis could be attempted using poly(cyclobutananthracene) (208) and another poly(acetylene) precursor, e.g. (204), which would produce a mixed pre-polymer, and could allow better elimination of anthracene.

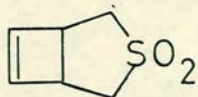
This work has considerable potential and further research is currently underway.

In passing, it is worth noting that similar attempts to

metathesise the strained hydrocarbon 5,6:7,8-dibenzobicyclo-[2.2.2]octa-2,5,7-triene, with both $\text{WCl}_6/\text{Me}_4\text{Sn}$ and $\text{MoCl}_5/\text{Me}_4\text{Sn}$, but both reactions ended in failure. This was not totally unexpected¹⁶⁰ since (37) contains a cyclohexene ring and, if reaction did occur, it would involve the formation of a highly hindered polymer (209).



As part of this study the metathesis of a number of other cyclobutene derivatives was also examined, but it was found that none of these reacted when either $\text{WCl}_6/\text{Me}_4\text{Sn}$ or $\text{MoCl}_5/\text{Me}_4\text{Sn}$ was used as catalyst. The compounds examined included cyclobutene anhydride (87) and the two sulphones (210) and (210a).¹⁶¹ both of which were originated in these laboratories. Further details of the chemistry of (210) will be discussed later in Section E.

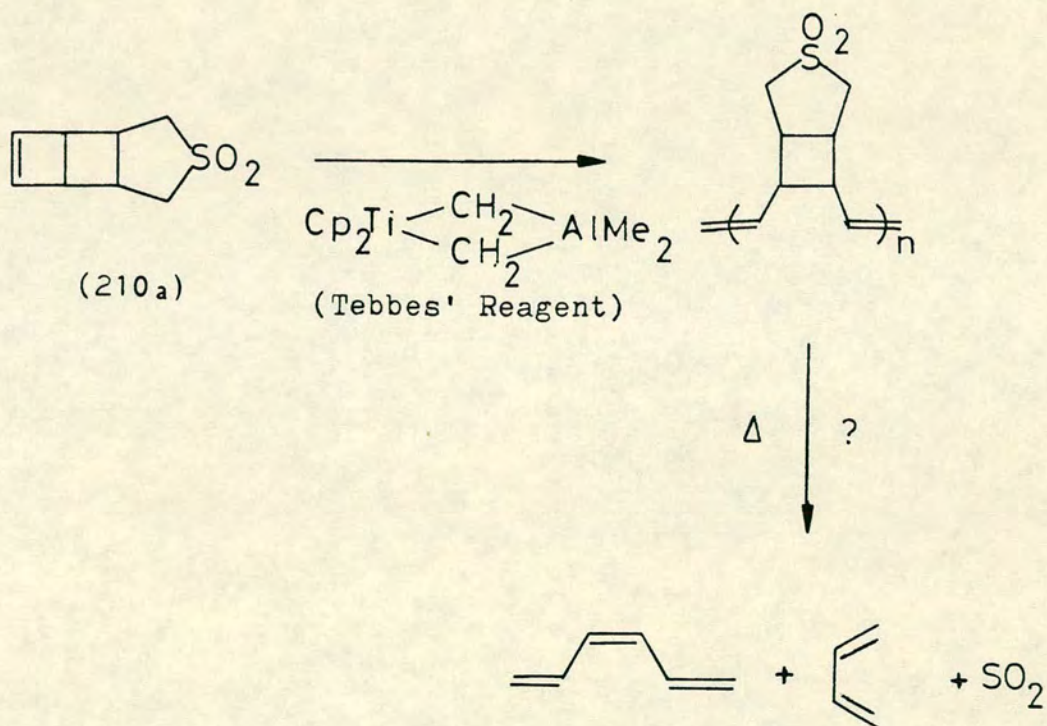


(210)



(210a)

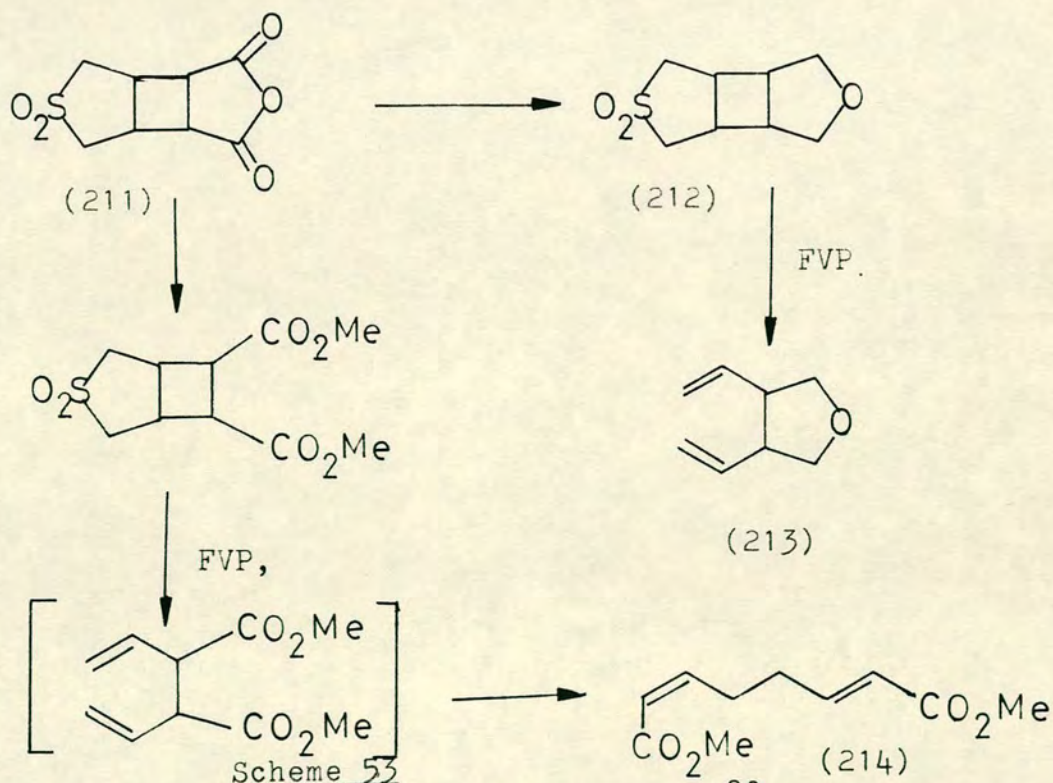
Wilkinson has postulated¹⁶² that such catalysts will complex with the p orbitals of the heteroatoms rather than the π orbitals of the alkene. As a result, this deactivates the catalyst and prevents metathesis of the strained cyclobutane ring. The lack of reaction in the above cases reinforces Wilkinson's proposals. Nonetheless some success has been achieved in the case of (210a) using Tebbes' Reagent.



E. Preparation and Pyrolysis of some Derivatives of
3-Thiabicyclo[3.2.0]hept-6-ene 3,3-Dioxide

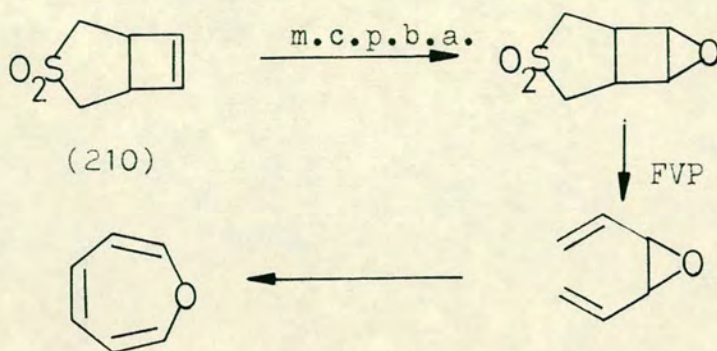
1. Background

The extrusion of SO_2 from cyclic molecules has found widespread use in the synthesis of a variety of hetero- and carbocyclic systems.^{62,163} In particular, work in these laboratories by McLaughlin⁸⁰ showed that cyclobutane-fused sulpholanes derived from the anhydride (211) formed the basis of useful synthetic methods for generating cis-1,2-divinyl compounds²⁵ (213) and acyclic diene derivatives (214)²⁶ as shown in Scheme 53.



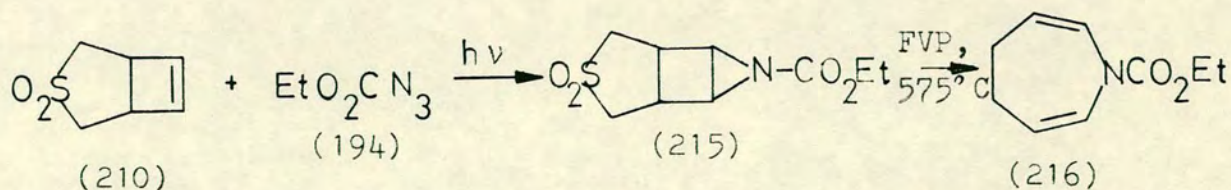
As part of these studies McLaughlin⁸⁰ also investigated the utility of the novel synthon, 3-thiabicyclo[3.2.0]hept-

6-ene 3,3-dioxide (210) as a means of generating cis-1,2-divinyl compounds which served as precursors to 7-membered heterocycles, for example Scheme 54.

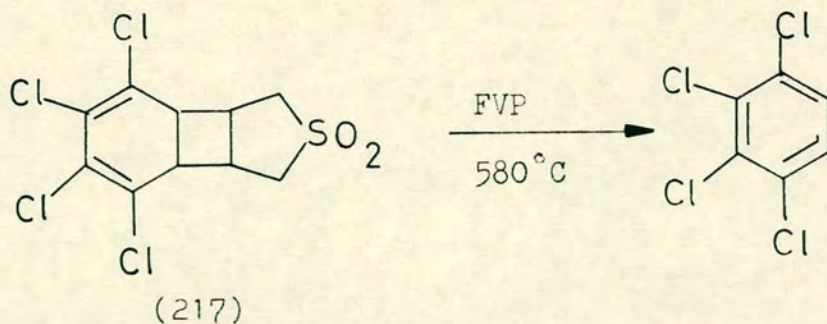


Scheme 54

Aitken⁸⁴ also showed that the corresponding aziridine (215) could also be formed by photolysis with ethyl azidoformate. Pyrolysis of compound (215) gave the corresponding dihydroazepine (216) albeit in 10% yield.



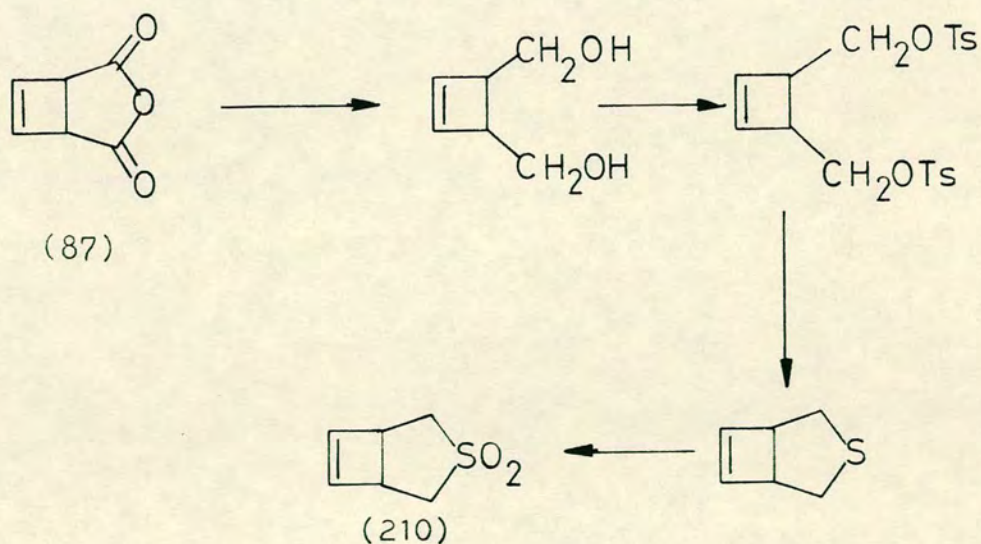
In a single example he also found that the sulphone (210) acted as an acetylene synthon. Thus reaction with the tetrachlorothiophen 1,1-dioxide (171) gave the adduct (217), pyrolysis of which caused cleavage to give the 1,2,3,4-tetrachlorobenzene.



This section details other reactions of (210) which have been examined in an attempt to determine the scope of its utility as an acetylene synthon.

2. Preparation of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

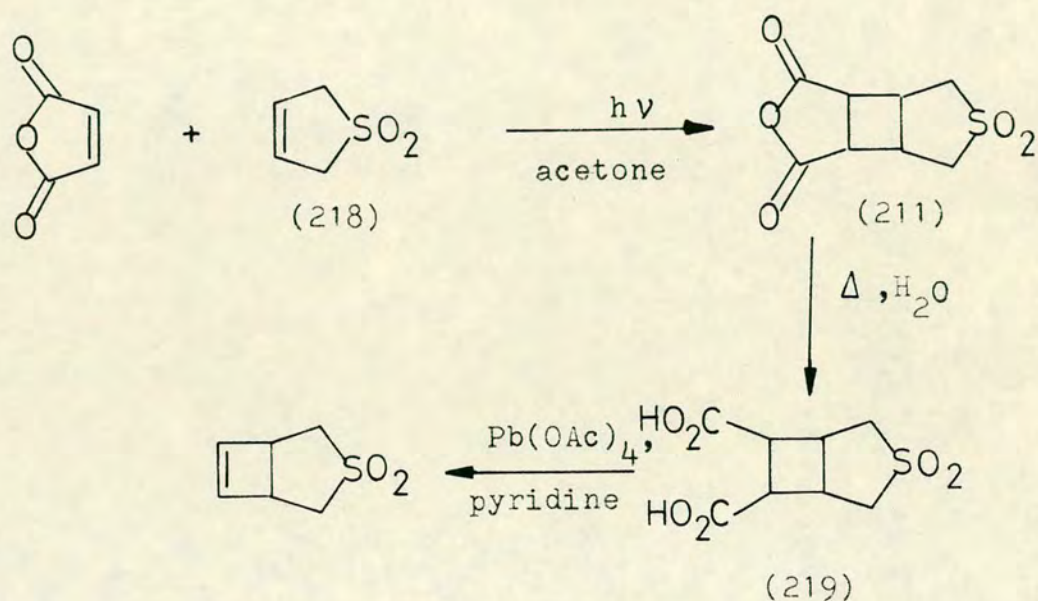
The alkene (210) could be obtained by two different routes, one of which involved the four stage synthesis using cyclobutene anhydride (87) as outlined in Scheme 55. This synthesis is discussed in more detail in Section F. The second route,



Scheme 55

which was that used by the author, involved the photochemical

addition of maleic anhydride with butadiene sulphone (218) to give the anhydride (211) which was easily converted into the diacid (219). Oxidative bis-decarboxylation of the latter with lead tetraacetate gave the desired sulphone in capricious yields.



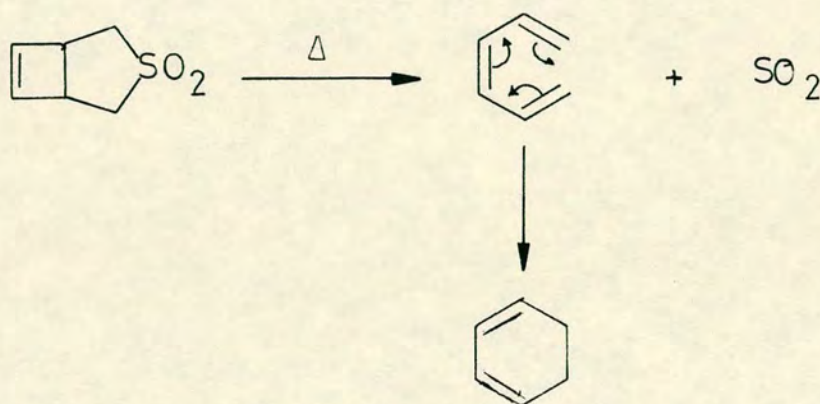
Scheme 56

Although the method of preparation of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide was similar to that used by McLaughlin, Scheme 56, an improvement was made to the synthesis in the oxidative bis-decarboxylation step by bubbling oxygen, rather than nitrogen, through the pyridine solution before the addition of the lead tetraacetate. In this way yields of greater than 20% were regularly recorded.

3. Preparation and pyrolysis of some derivatives of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

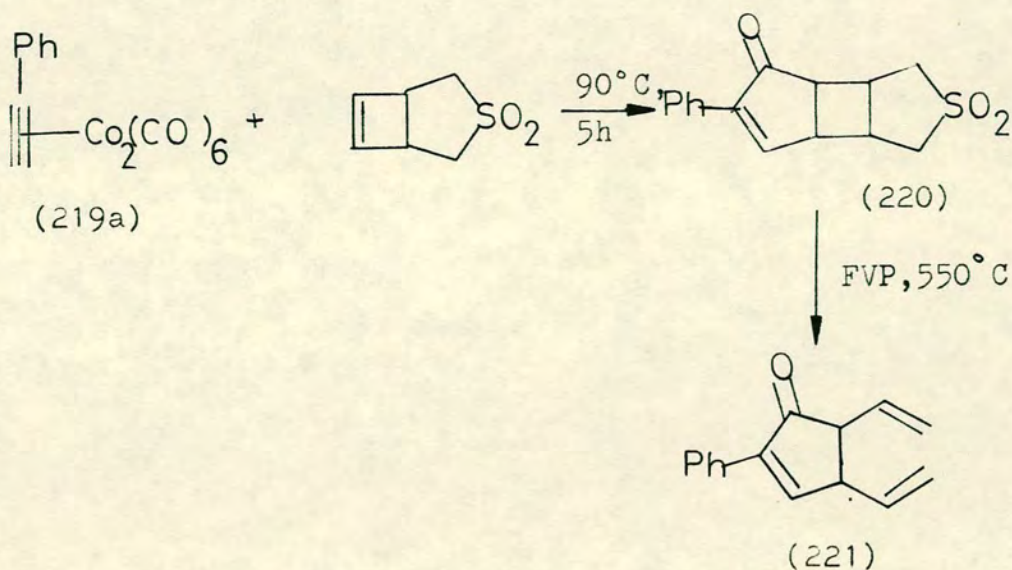
In initial experiments, attempts were made to react (210) with 1-piperidine^e 1-oxide in boiling toluene, but these ended

in failure with the recovery of unchanged alkene. The corresponding reaction of (210) with anthracene in boiling xylene was also unsuccessful. These reactions were not attempted at temperatures higher than 140°C since the sulphone (210) decomposed rapidly at higher temperatures to give cyclohexa-1,3-diene, as shown in Scheme 57.



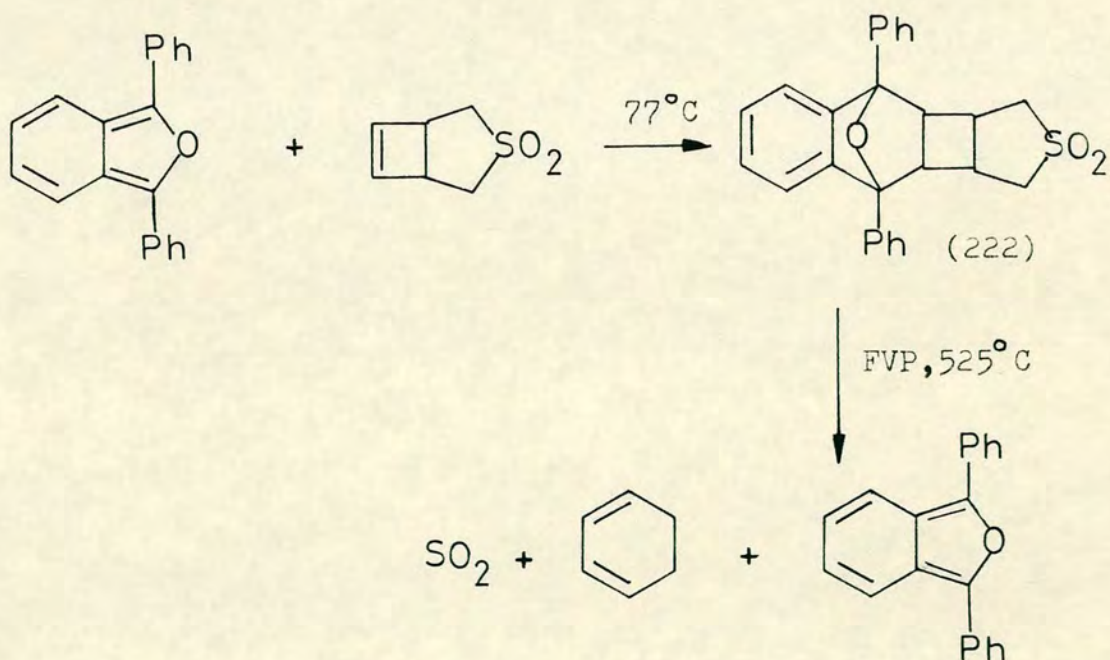
Scheme 57

In a collaborative study with Dr. D.C. Billington of the University of Strathclyde, the ketone (220) was successfully prepared in 65% yield by condensation of the sulphone (210) with the carbonyl cobalt acetylene complex (219a). As in the case of the furan derivative (212) pyrolysis of this adduct at 550°C gave a product (60%) as a liquid which



was difficult to purify due to its ready decomposition during column chromatography. Nonetheless the ^1H -n.m.r. spectrum of the crude product showed peaks between $\delta 5.0$ and $\delta 6.0$ indicative of the expected cis-1,2-divinyl compound (221). The mass spectrum of the crude product gave a peak, m/z 210, which was the expected value for the divinyl compound (221). It is worth noting that other workers in these laboratories have also recorded the decomposition of cis-1,2-divinyl compounds during attempted purification by column chromatography.

The corresponding reaction of the sulphone with 1,3-diphenylisobenzofuran in boiling benzene gave the adduct (222) in a yield of 25% as colourless needles. The pyrolysis of



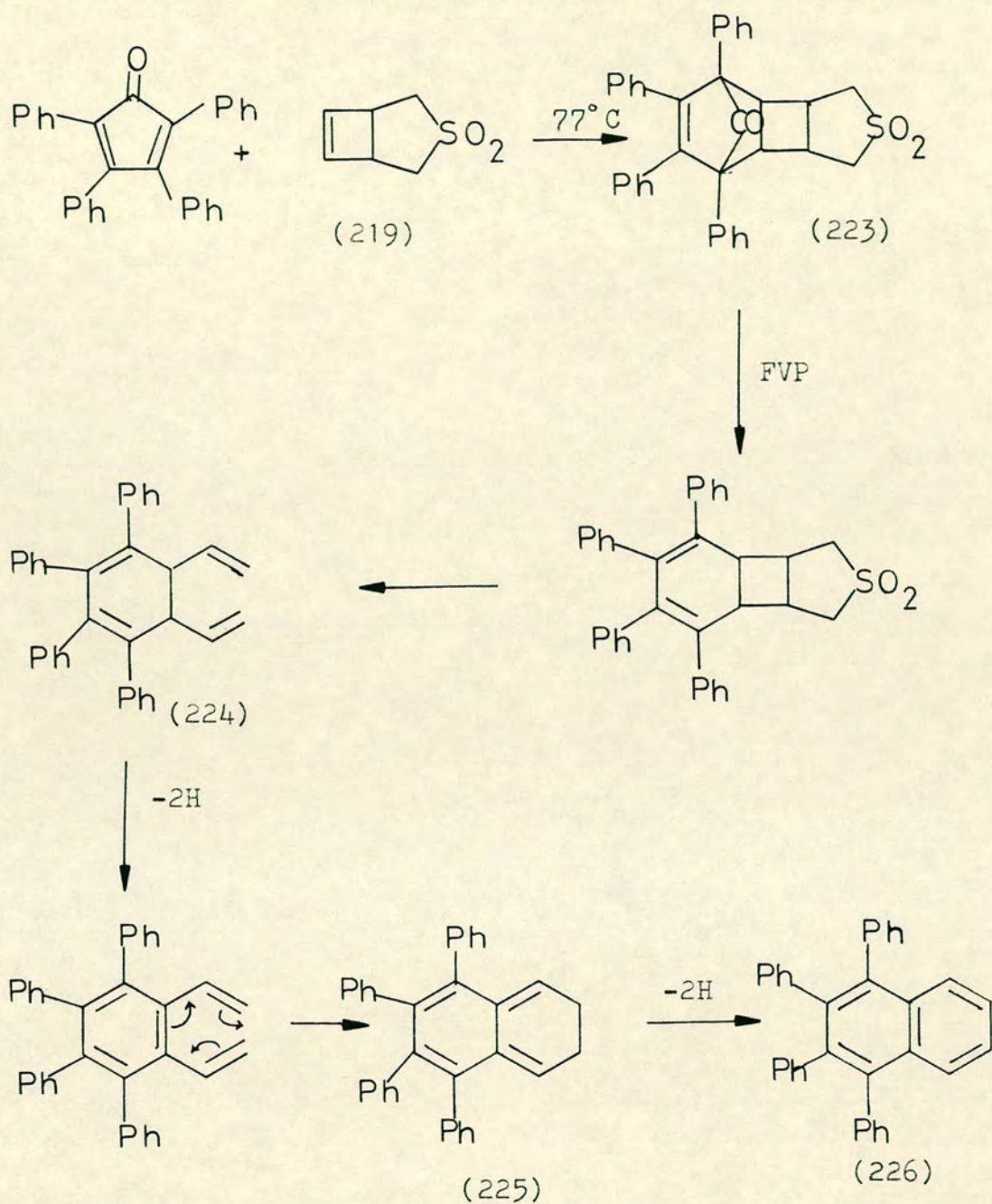
this adduct at 525°C resulted in a retro-reaction and only 1,3-diphenylisobenzofuran was isolated. Presumably the concomitant sulphone underwent fragmentation to SO_2 and the highly volatile cyclohexa-1,3-diene as described above.

Likewise the Diels-Alder reaction of the sulphone (210) with tetraphenylcyclopentadienone also proceeded readily but the pyrolysis of the adduct gave unexpected results, details of which are discussed in the following section together with those obtained for the pyrolysis of the corresponding adduct derived from cyclobutanthalene .

4. Preparation and pyrolysis of tetracyclone adducts of 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide and cyclobutanthalene

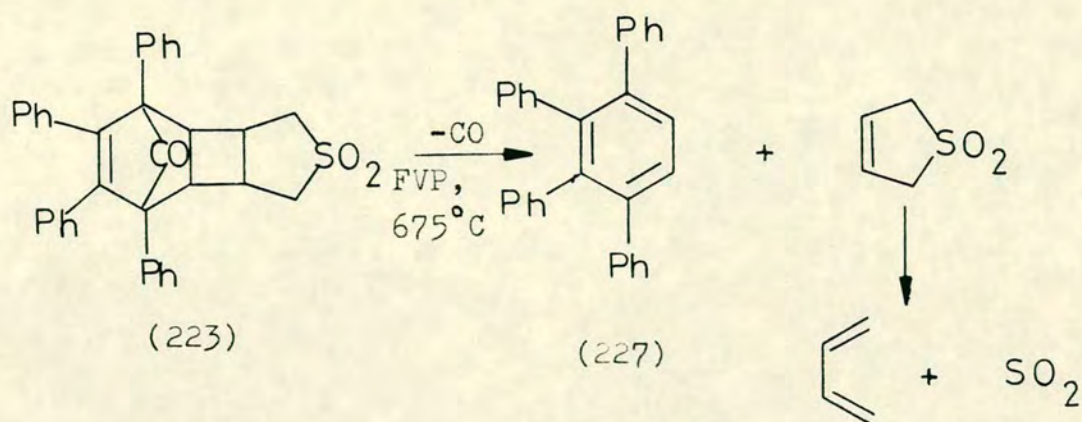
The reaction between the sulphone (219) and tetracyclone took place in boiling benzene to give a colourless solid in 55% yield. Spectroscopic examination and analytical data showed it to be the expected adduct (223) in which the carbonyl moiety remained intact. It was envisaged that F.V.P. of this compound would lead to initial extrusion of CO, followed by loss of SO₂ to give the divinyl product (224). The latter would either be stable or, more likely, lose hydrogen to form (225) which could then undergo electrocyclisation to give 1,2,3,4-tetraphenylnaphthalene (226) after further loss of hydrogen.

In actuality F.V.P. of the adduct (223) at 675°C gave a yellow solid the ¹H-n.m.r. spectrum of which showed it to be wholly aromatic in nature. The product was purified by preparative t.l.c. to give essentially pure 1,2,3,4-tetraphenylbenzene (227) as evidenced by comparison with an authentic sample. Clearly, in this case the sulphone (210) was acting

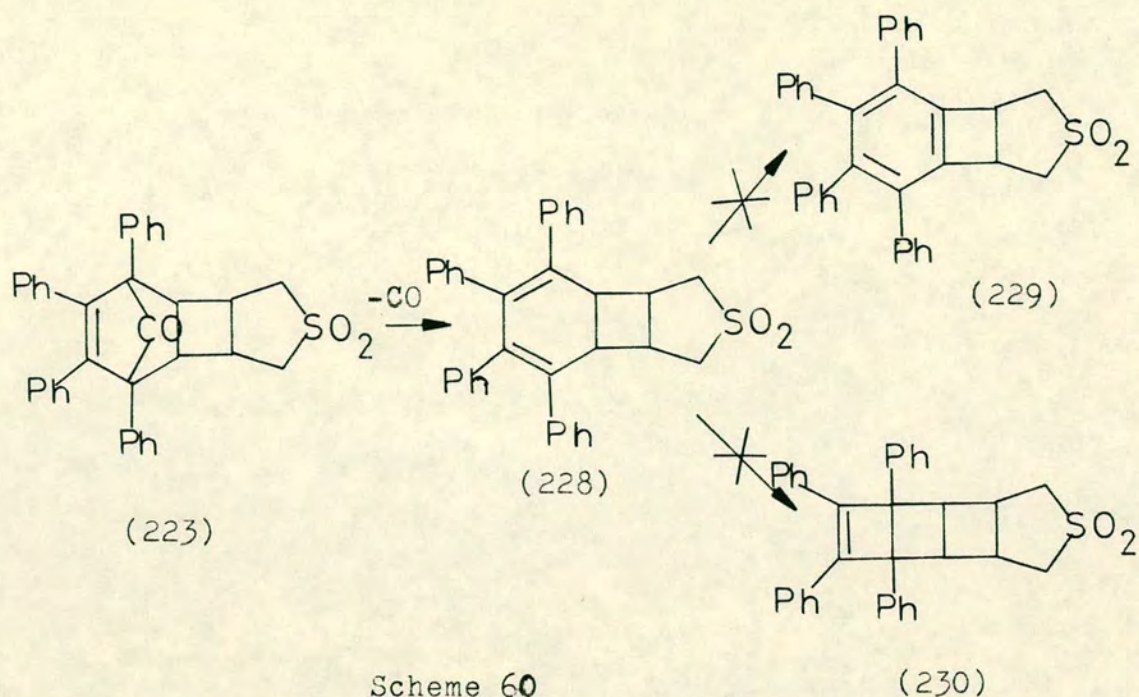


Scheme 58

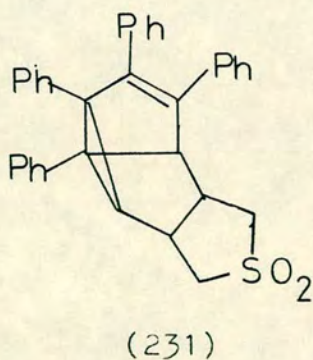
as an acetylene synthon. As shown in Scheme 59, the adduct (223) apparently cleaved, presumably after losing carbon monoxide to give butadiene sulphone which fragmented under the reaction conditions. The driving force of this cleavage is undoubtedly a consequence of the formation of the benzene ring.

Scheme 59

In an attempt to prevent the extrusion of butadiene sulphone, the temperature of the pyrolysis was lowered. At temperatures greater than 500°C 1,2,3,4-tetraphenylbenzene was the exclusive product of fragmentations. By lowering the temperature to 350°C , the outcome was the exclusive extrusion of carbon monoxide to give a colourless solid, m.p. 274°C . The i.r. spectrum of this compound was characterised by the absence of a carbonyl absorption and the presence of distinctive sulphone peaks at 1315 and 1140 cm^{-1} . At first, it was thought that the compound possessed structure (228) but its ^1H -n.m.r. spectrum showed a total of only seven aliphatic protons as opposed to the expected number of eight for (228). Additionally four of these were attached to the carbons α to the sulphone group. This fact also excluded structure (229) which might be formed by aromatisation as well as the tetracyclic structure (230), derived from (228) by ring contraction. This was corroborated by ^{13}C -n.m.r. spectroscopy which clearly indicated a lack of symmetry in the compound. As shown in Fig. 11, the spectrum showed the presence of two

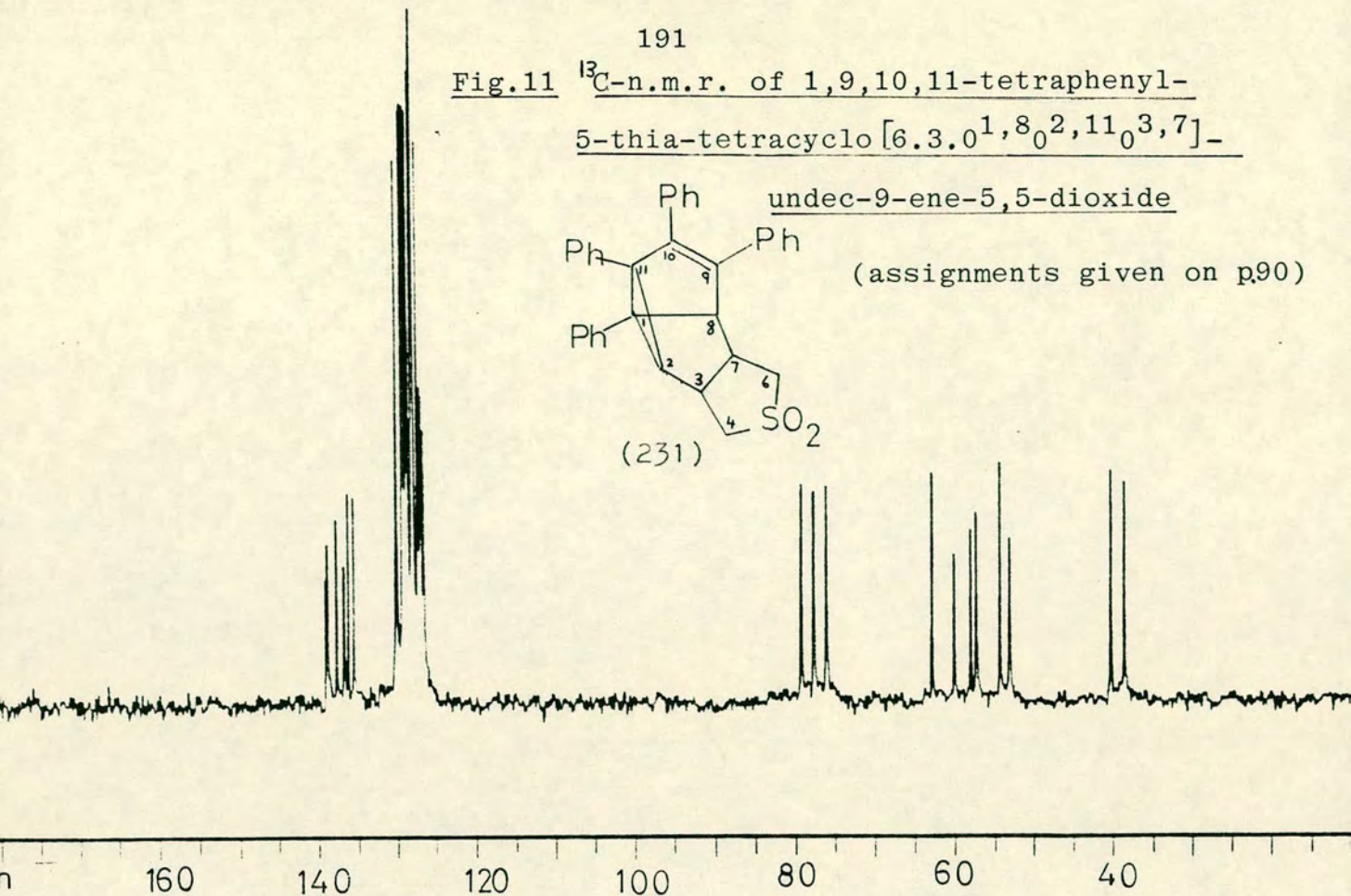
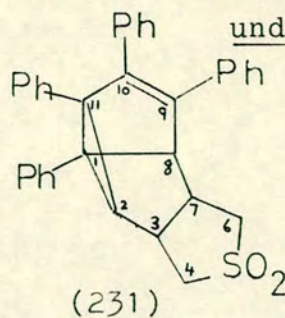


quaternary and six aliphatic carbons, as well as four carbons linked to phenyl rings and two olefinic carbons. This information coupled with the ^1H -n.m.r. spectrum provided firm evidence for dihydrosemibullvalene structure (231).

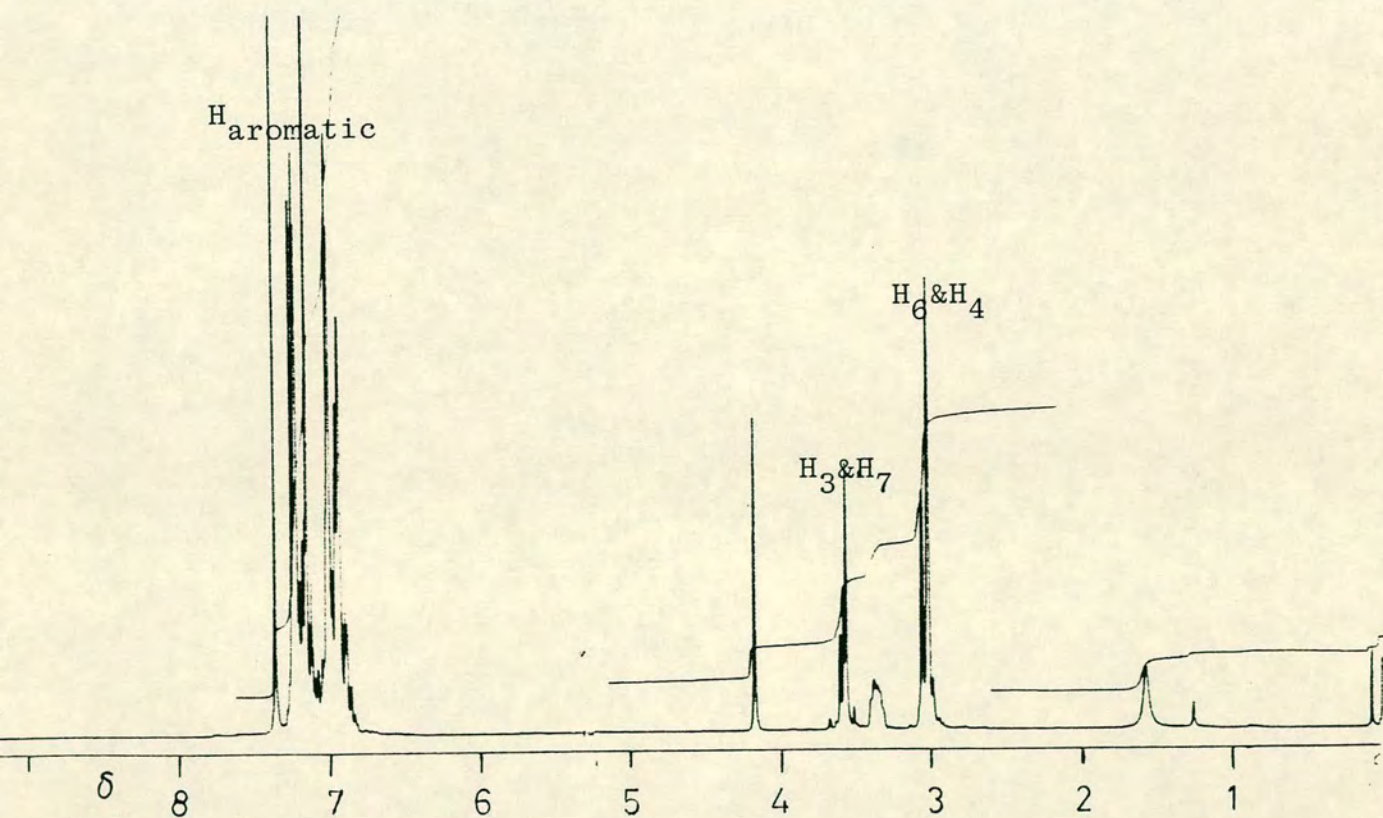


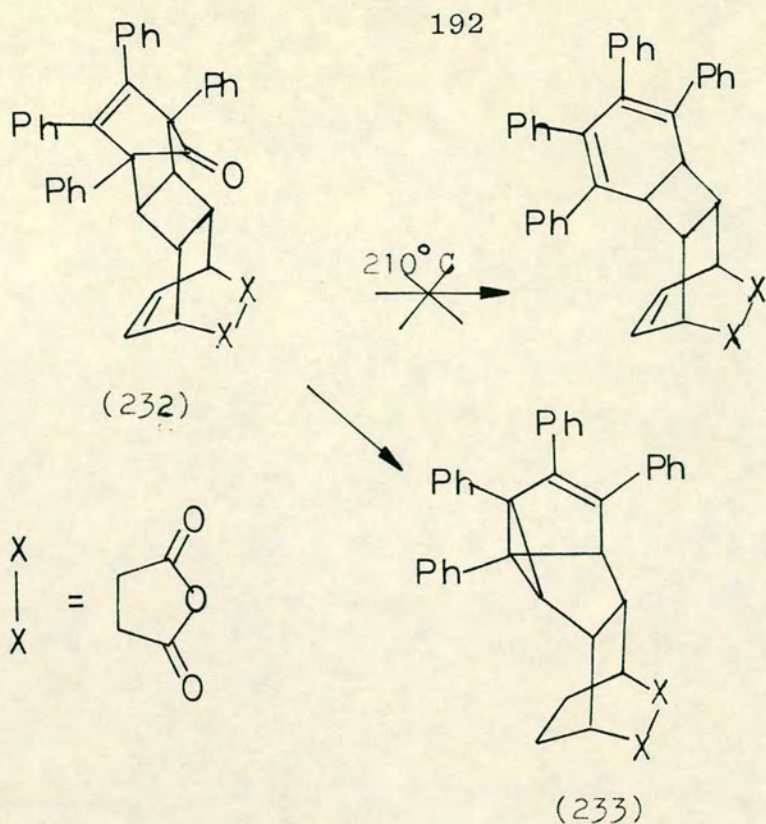
This is substantiated by the studies of Fray and Mackenzie et al.¹⁶⁴ who found that thermolysis of the cyclopentadienone adduct (232) gave rise to a dihydrosemibullvalene (233) which was confirmed by X-ray analysis.

Fig.11 ^{13}C -n.m.r. of 1,9,10,11-tetraphenyl-
5-thia-tetracyclo[6.3.0^{1,8}₀^{2,11}₀^{3,7}]-



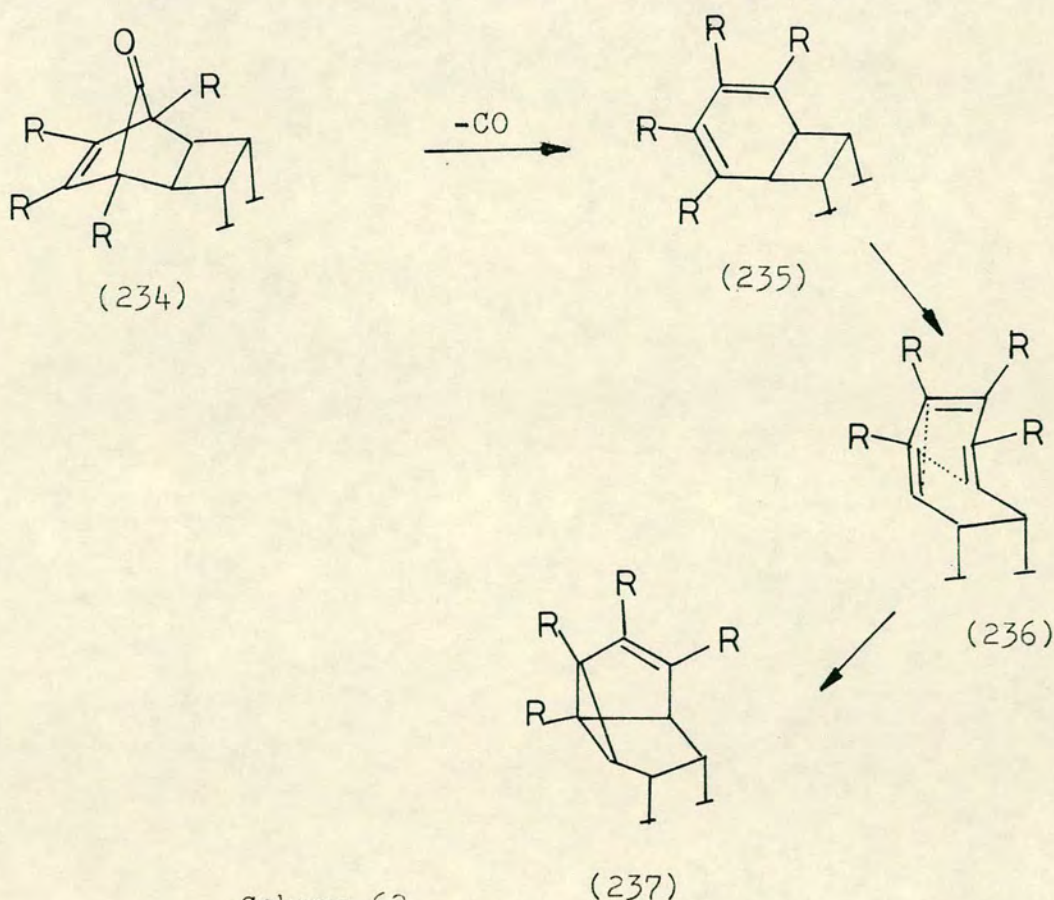
^1H -n.m.r. of (231)





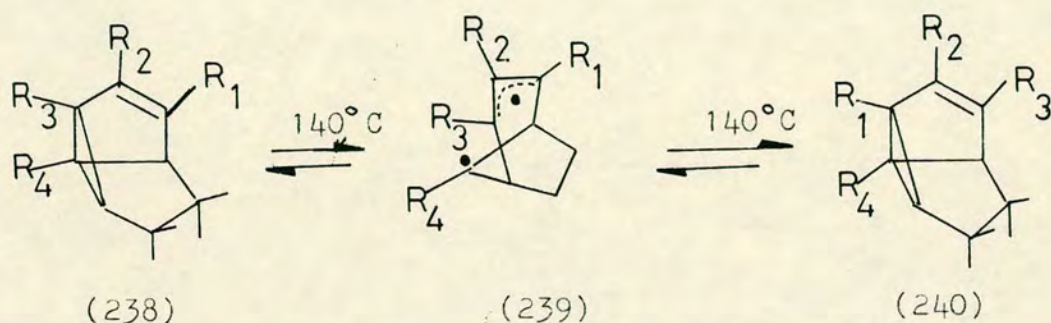
Scheme 61

The formation of (231) can be rationalised by the mechanism outlined in Scheme 62 whereby ring opening of (235) occurs to give the bicycloocta-2,4,6-triene (236) which collapses to (237) as indicated. It is thought that the



Scheme 62

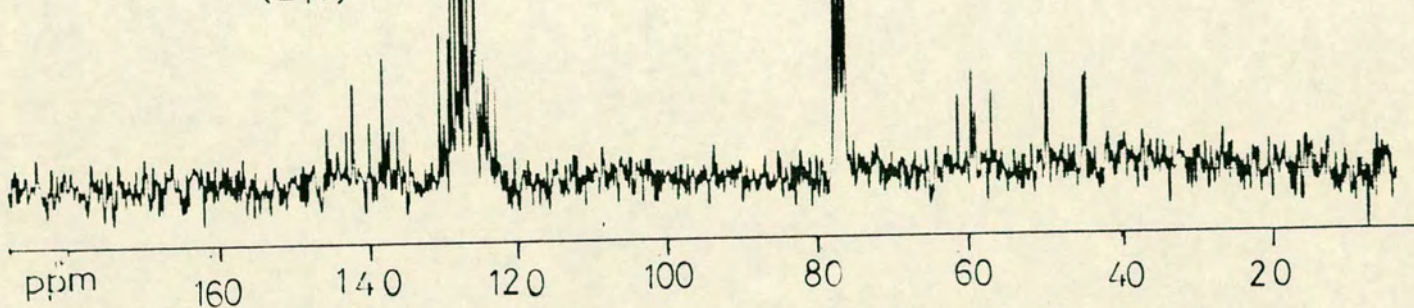
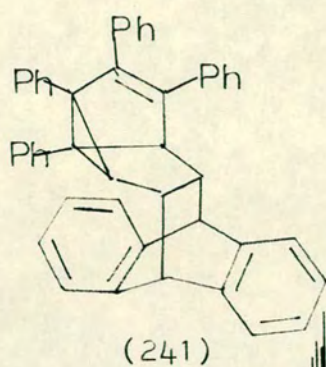
formation of the arylated dihydrosemibullvalene (237) is due to a thermally allowed ($\pi_4 + \pi_2$) cycloaddition in the cyclooctatriene ring system which is formed by a 6π electrocyclic reversion of the relevant bicyclo[4.2.0]octadiene (235). In further experiments Greenfield and Mackenzie¹⁶⁸ discovered a facile isomerisation of the resulting dihydrosemibullvalenes, e.g. (238) \rightleftharpoons (240) via (239)



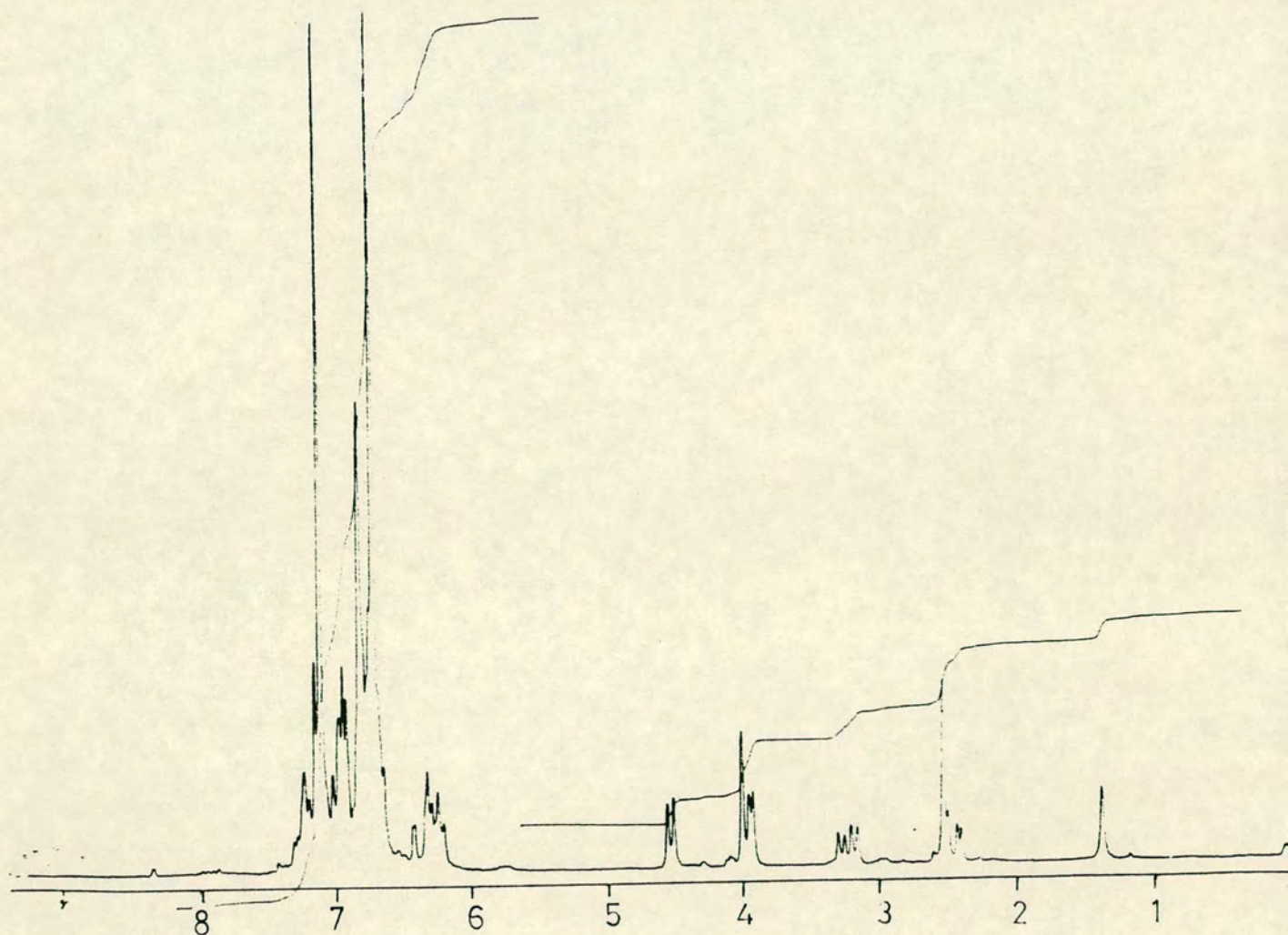
Obviously in the present work, which involved only the tetraphenyldihydrosemibullvalene, no such rearrangement could be observed.

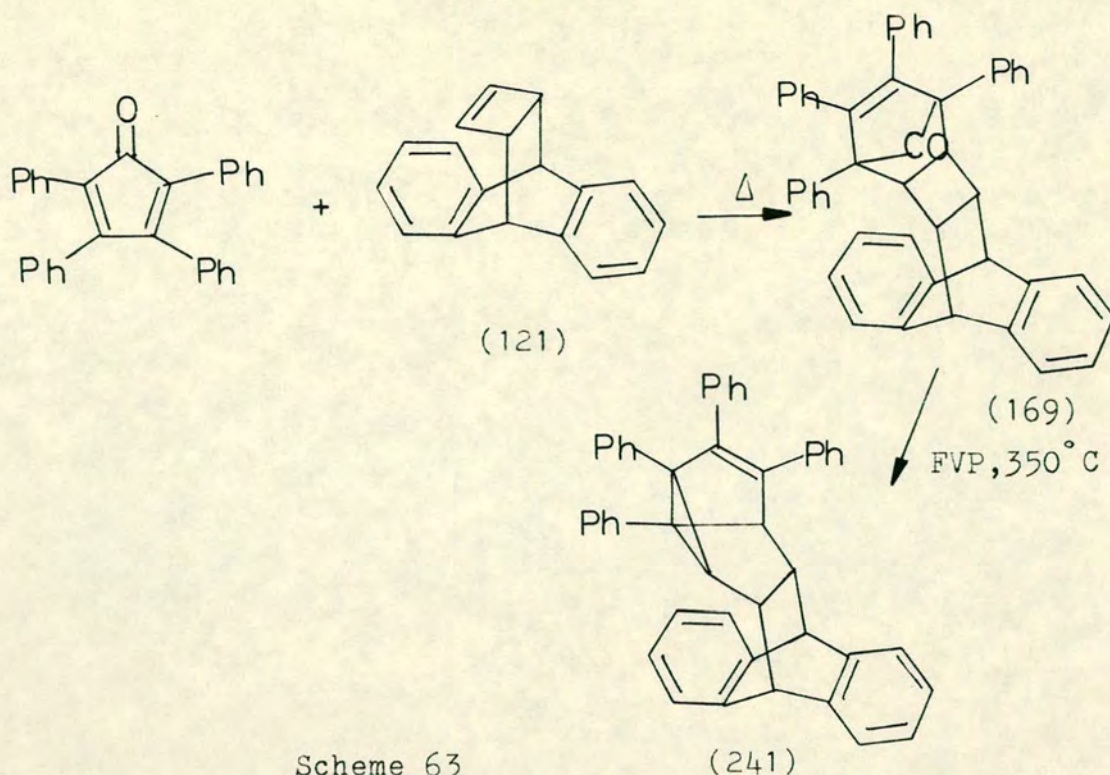
Similarly, the adduct (183) formed by the reaction of tetracyclone with cyclobutananthracene (169) yielded colourless solid (63%) upon F.V.P. at 350°C. That the loss of CO had occurred was confirmed by its i.r. spectrum which showed the absence of a carbonyl absorption. This evidence together with analytical data suggested the similar formation of a dihydrosemibullvalene (241) which was confirmed by ¹³C-n.m.r. spectroscopy. Indeed comparison of its ¹³C-n.m.r. spectrum (Fig. 12) with that of the dihydrosemibullvalene (231) showed a remarkable similarity.

Fig.12 ^{13}C -n.m.r. of 4,5,6,7-tetraphenyl-11,12:13,14-dibenzo-pentacyclo[8.2.2.0^{2,9}.0^{3,7}.0^{4,8}]tetradeca-6,11,13-triene



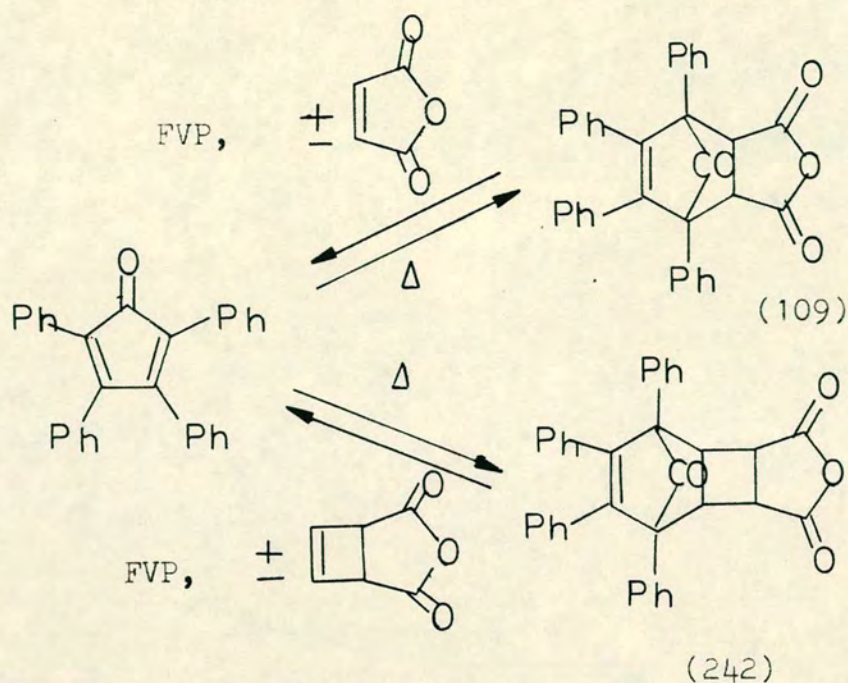
^1H -n.m.r. of (241)





Scheme 63

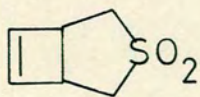
Following these results, other tetracyclone adducts, e.g. (109) and (242) were also pyrolysed under F.V.P. conditions. Spectroscopic analysis of the products showed that in these cases, pyrolysis at 350°C did not result in the formation of dihydrosemibullvalenes. Instead, cycloreversion occurred to give starting materials. Apparently both the sulphone (210) and cyclobutananthracene (121) are not as good a leaving group as CO in thermal processes whereas, maleic anhydride and cyclobutene anhydride are clearly better.



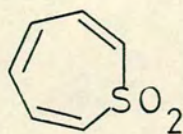
Scheme 64

5. Bromination and dehydrobromination of 3-thiabicyclo-[3.2.0]hept-6-ene 3,3-dioxide

In principle, 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (210) is a possible starting material for the synthesis of thiepin-1,1-dioxide (243) on the basis that both sulphones have similar structures of six carbons and a sulphone group but with different oxidation levels.



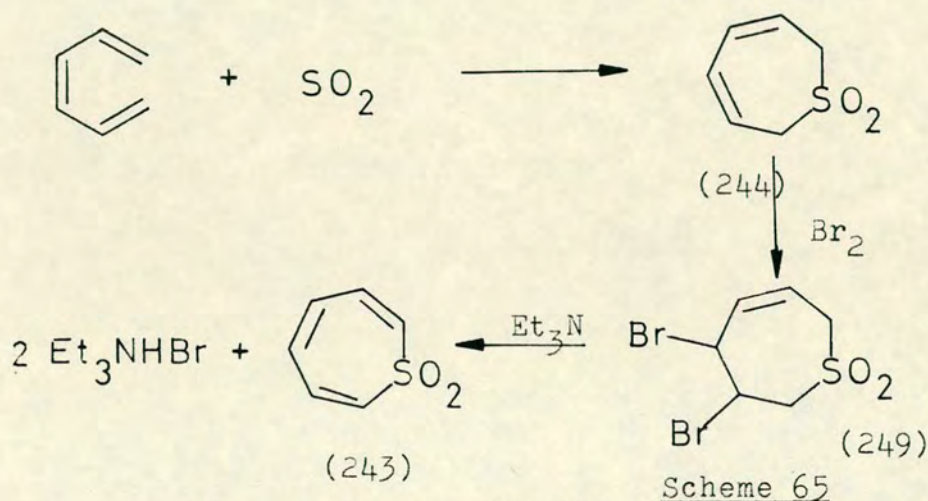
(210)



(243)

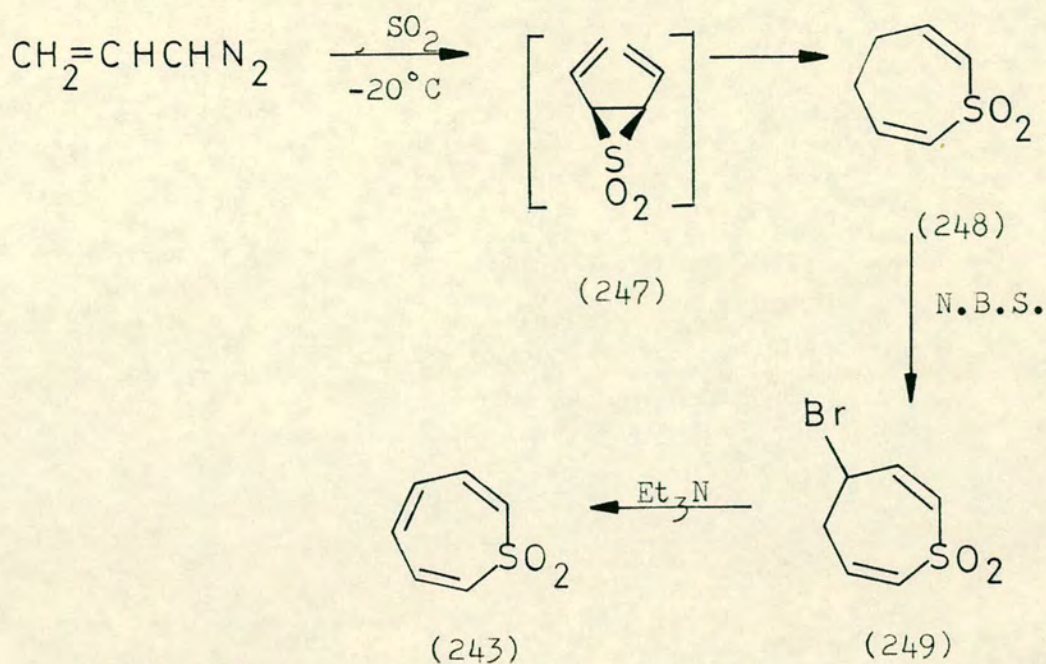
Thiepin-1,1-dioxide (243) is a molecule of much interest,¹⁷⁰ being a conjugated cyclic sulphone whose properties have not been fully investigated. Two routes to thiepin-1,1-dioxide

have been reported already, the first of which was described by Mock *et al.*¹⁷⁰ in 1967. This synthesis, shown in Scheme 65, involved the addition of sulphur dioxide to *cis*-hexatriene at room temperature to form 2,7-dihydrothiepin-1,1-dioxide (244). Treatment of (244) with bromine gave the dibromide (245), dehydrobromination of which afforded the thiepin-1,1-dioxide (243).

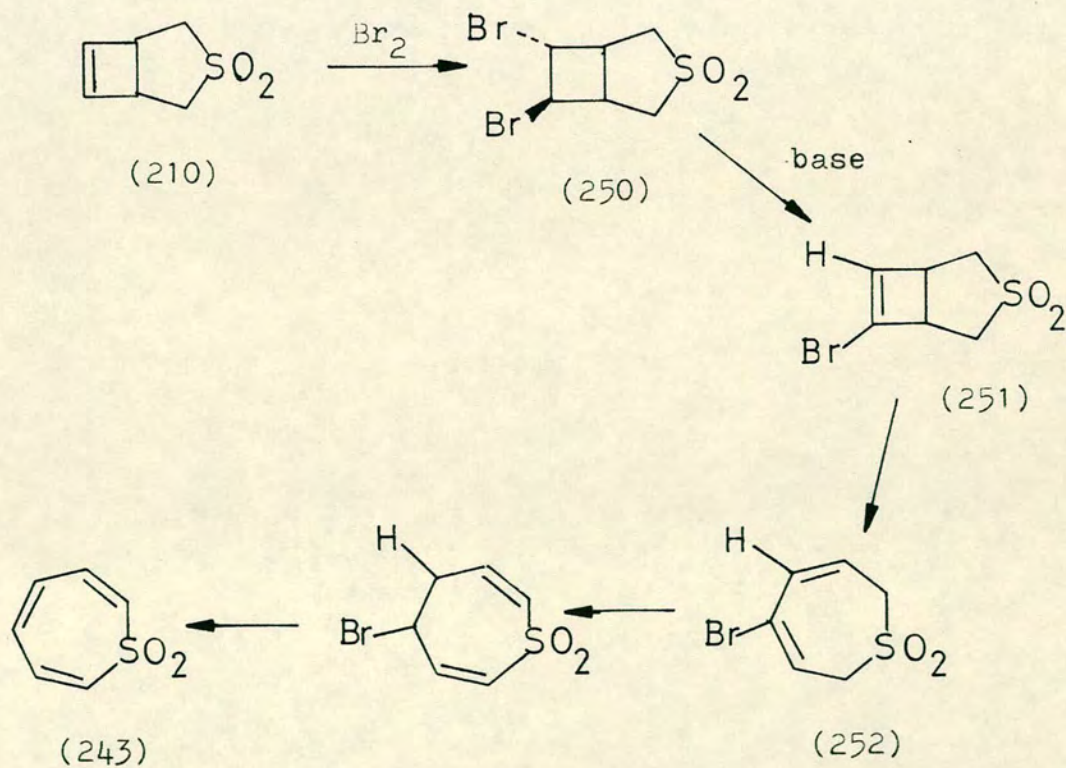


Paquette and co-workers^{171,172} subsequently reported an alternative method which involved the slow addition of sulphur dioxide to a solution of vinyl diazomethane at -20°C to give 4,5-dihydrothiepin-1,1-dioxide (248) via the intermediate episulphone (247). Allylic bromination of (248) with *N*-bromosuccinimide afforded (249) which on treatment with triethylamine gave thiepin-1,1-dioxide (243) in 40% yield.

For sulphone (210) to be transformed into thiepin-1,1-dioxide (243) requires ring-opening with loss of hydrogen. This might be accomplished by bromination of the sulphone (210) and subsequent dehydrobromination as shown in Scheme 67.

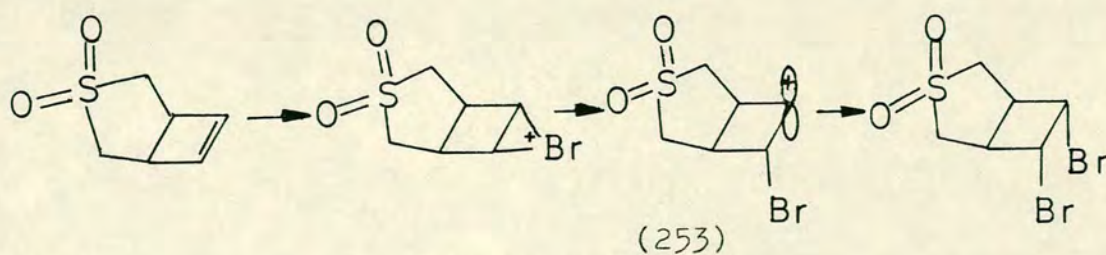
Scheme 66

Elimination of HBr from (250) would, through necessity, have to proceed via its base-catalysed isomer (252).

Scheme 67

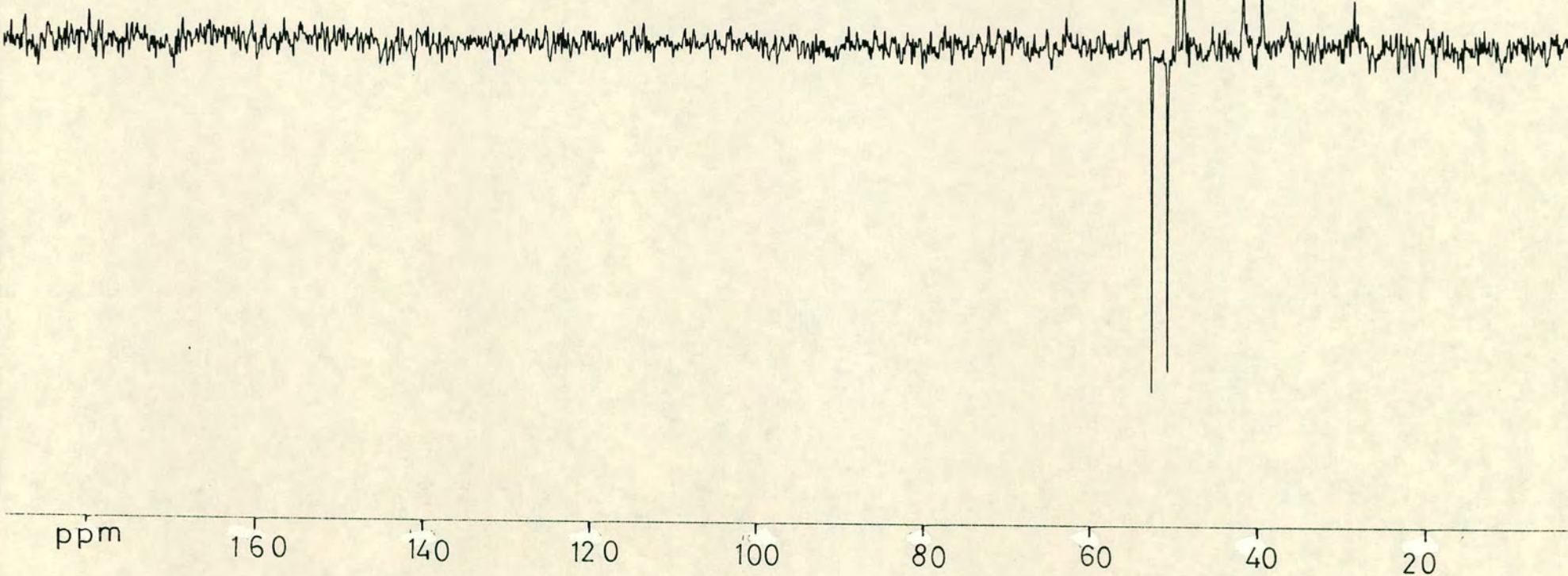
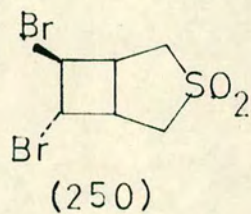
The bromination of the sulphone (250) was easily accomplished by heating with bromine in boiling carbon tetrachloride for 19h to give an 86% yield of the expected trans-isomer (250)* see fig.13 for ^{13}C -n.m.r. However, its dehydrobromination proved to be more difficult than expected. Several conditions were employed including the addition of triethylamine to a benzene solution at 20°C ³¹ but no reaction was observed even upon heating under reflux. Likewise no reaction occurred when sodium hydroxide was added to the dibromide (250) in tetrahydrofuran and the solution boiled under reflux overnight. Elimination of one mole of HBr was eventually achieved using potassium t-butoxide in dimethoxyethane at 20°C . Under these conditions monobromoalkene (251) was formed in 74% yield. When the reaction was

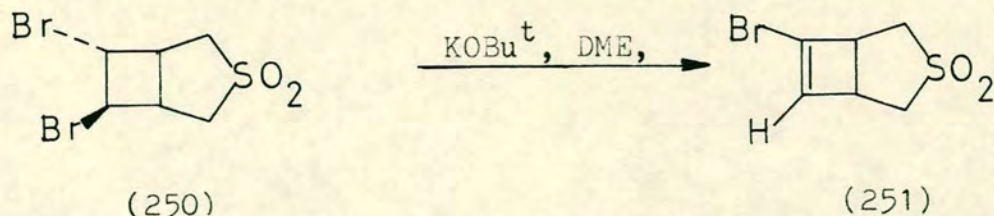
* Further investigations of this reaction in these laboratories¹⁷³ have shown that bromination under different conditions can also give rise to the cis-isomer. It is believed that this is a consequence of orbital interactions through space which stabilise a discrete carbonium ion (253), Scheme 68.



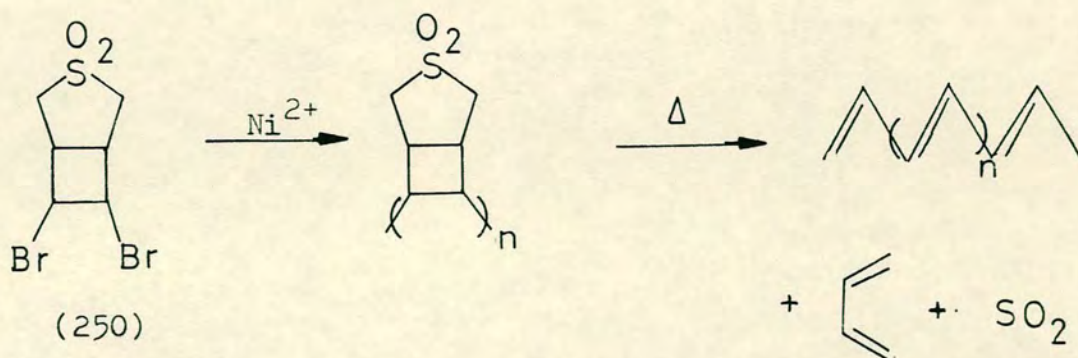
Scheme 68

Fig.13 ^{13}C (INEPT) n.m.r. of e E-6,7-dibromo-3thiabicyclo 3.2.0 heptane-3,3-dioxide





carried out at 50°C , charring occurs and a much lower yield of (251) resulted. Further attempts were made to effect complete dehydrobromination of (251) using sodium methoxide at 50°C but no reaction took place even after 36h. A hindered base, D.B.U. similarly failed to effect dehydrobromination, as did lithium diisopropylamide under forcing conditions. In view of these failures it was decided to ring-open the molecule prior to dehydrobromination but efforts to cause this rearrangement both with Ag^+ and by photolysis were not successful. As a result this approach to thiepin-11-dioxide was abandoned but it is worth pointing out that the dibromo compound (250) is now under investigation as a precursor to poly(acetylene), Scheme 69.

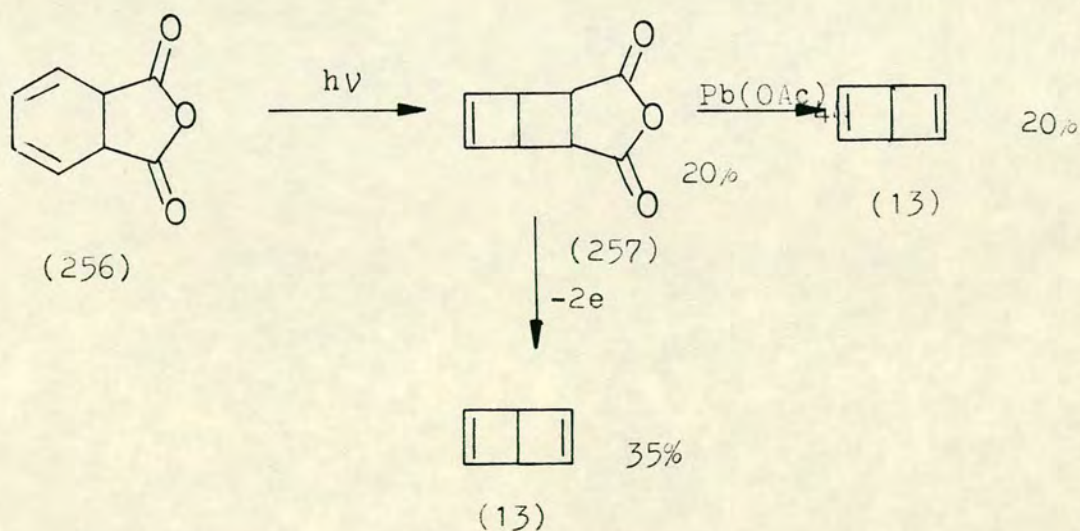


Scheme 69

F. A New Approach to Bicyclo[2.2.0]hexa-2,5-diene (Dewar Benzene) from 2-Chloro-3-thiabicyclo[3.2.0]hept-6-ene 3,3-Dioxide

1. General background

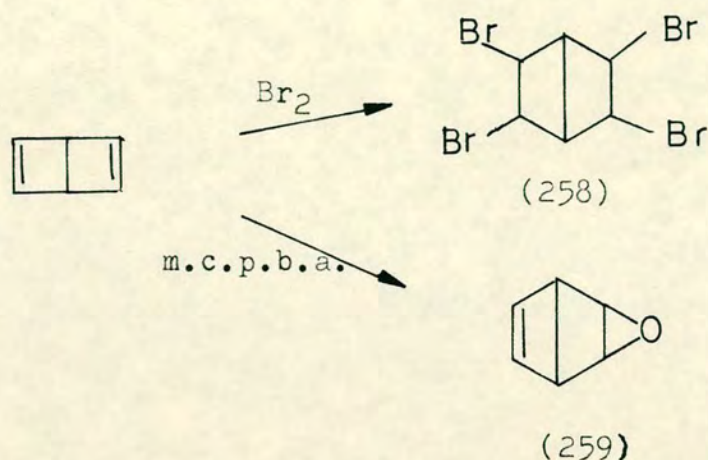
Following almost a century of speculation as to its existence, Dewar benzene (13) was first synthesised by van Tamelen and co-workers¹⁷⁴ in the late 1960's. Their method involved the irradiation of cis-1,2-dihydrophthalic anhydride (256) at -20°C to form the tricyclic anhydride (257) which could be oxidatively decarboxylated with lead tetraacetate to give this elusive compound albeit in 20% yield. The yield of this final step was subsequently increased to 35% by electrolytic decarboxylation of the corresponding diacid.



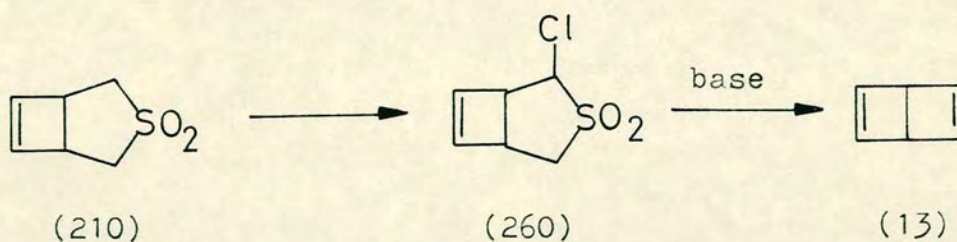
Scheme 70

Despite the instability of Dewar benzene ($t_{1/2} = 48\text{h}$ at 20°C , 90min at 90°C) the compound was obtained in pure form and was characterised by reaction with several reagents,¹⁷⁴ including bromine to give a complex mixture of stereoisomeric

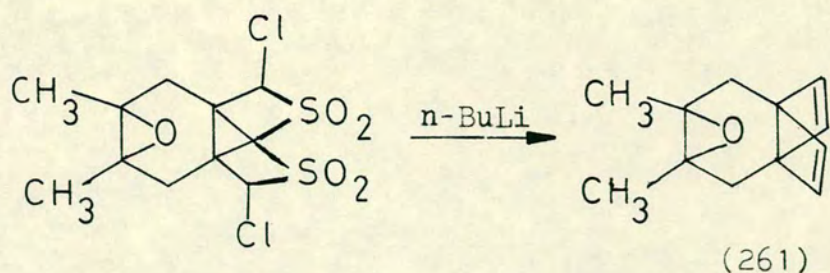
tetrabromides (258) and m-chloroperoxybenzoic acid which led to the formation of the epoxide (259).



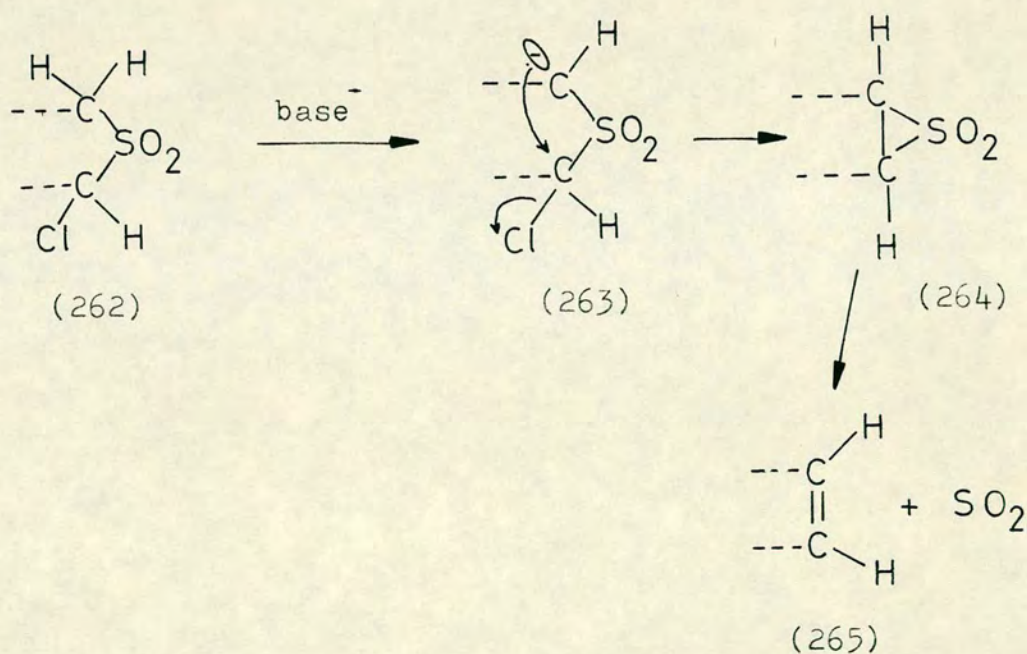
No other synthesis of Dewar benzene has since been reported but interest in these laboratories in the chemistry of the 3-thiabicyclo[3.2.0] ring system prompted an investigation of its suitability as a new source of this interesting compound. In the approach adopted the key step involved a base-induced decomposition of the α -chloro-sulphone (260) by means of a Ramberg-Bäcklund reaction.



The Ramberg-Bäcklund reaction has been extensively investigated by Paquette et al.¹⁷¹ and has been utilised in several syntheses of highly strained propelladienes^{175-177,120,121,140} e.g. (261). In its initial step, the reaction involves the



generation of a carbanion α to the sulphone group (263). This collapses with loss of chloride ion. The negative charge causes elimination to form an episulphone (264) which quickly loses sulphur dioxide and forms a carbon carbon double bond (265), details are given in Scheme 71.

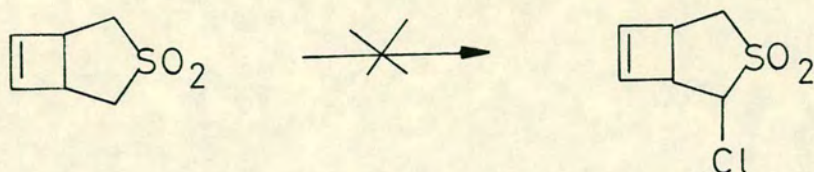


Scheme 71

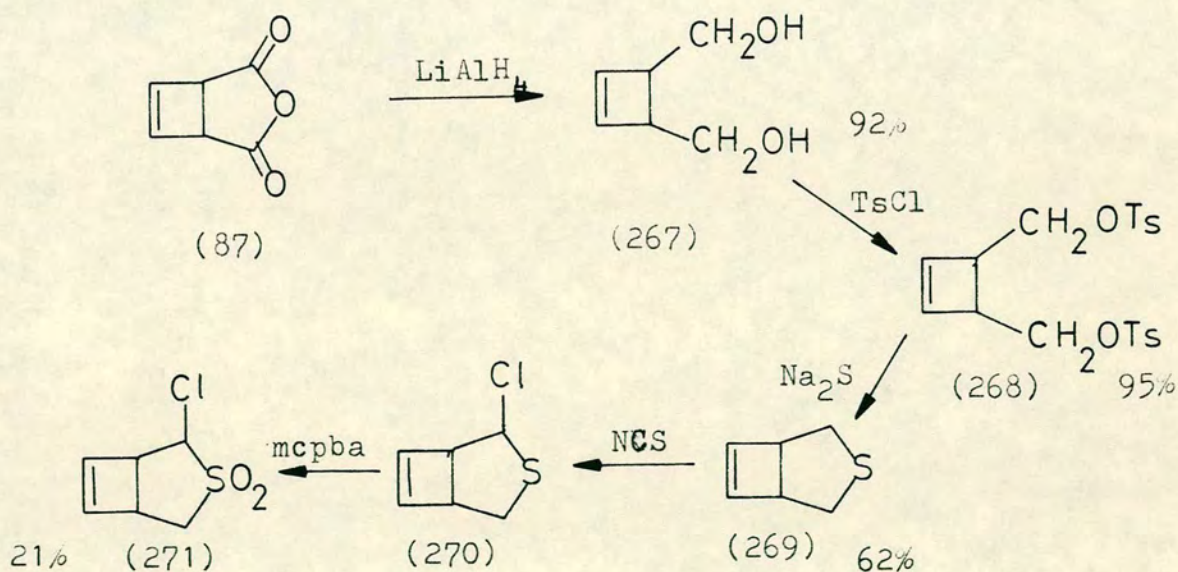
2. Preparation of 2-chloro-3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide

In exploratory studies, it was found that 3-thiabicyclo[3.2.0]hept-6-ene 3,3-dioxide (210) could not be chlorinated

directly in the position α to the sulphone group. As a consequence it was necessary to use a different approach



involving free radical chlorination of 3-thiabicyclo[3.2.0]-hept-6-ene (269), followed by oxidation to give the desired sulphone. The overall synthetic strategy is outlined in Scheme 72,



Scheme 72

The preparation of (87) has been discussed fully in Section A.

The synthetic stages up to the sulphide (269) were both simple and efficient to give a high yield of (269). It was

necessary to chlorinate the sulphide (269) prior to oxidation to the sulphone; this was achieved with N-chlorosuccinimide. Following oxidation with m-chloroperoxybenzoic acid the α -chloro sulphone (271) was obtained in 21% overall yield. This material was used as the starting material for the Ramberg-Bäcklund reaction.

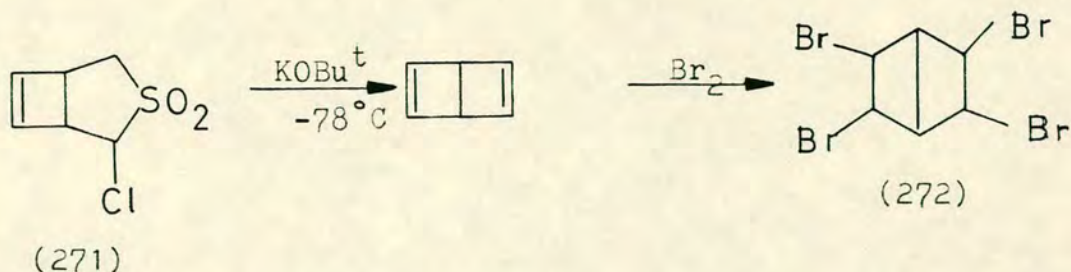
3. Synthesis and trapping of Dewar benzene

Since Dewar benzene is temperature sensitive it was necessary to use a strong base which would preclude the use of elevated temperatures to effect the reaction. Potassium *t*-butoxide at temperatures of -30. to -78°C had been used successfully by Weinges et al.^{175,176} for the synthesis of propelladienes.

The α -chlorosulphone (271) was treated with potassium *t*-butoxide and after the work up the products were analysed by g.l.c. This analysis revealed that only tetrahydrofuran and pentane, solvents used in the reaction and work up, were present.

Van Tamelen et al. had previously brominated Dewar benzene to give the essentially pure tetrabromide (272) as a white crystalline solid but also found a complex mixture of di- and tetrabromide isomers when equimolar amounts of Dewar benzene and bromine were reacted.

In the synthesis shown in Scheme 73 the product obtained from the bromination was a dark brown free flowing oil which could not be column chromatographed. The ¹H-n.m.r. spectrum



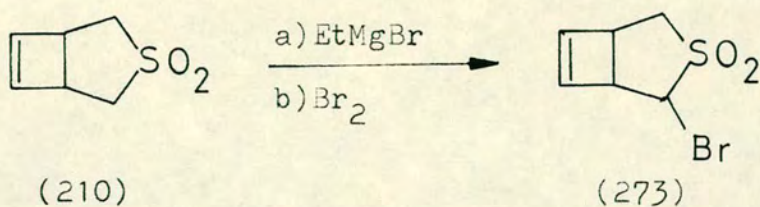
Scheme 73

of the oil showed several broad peaks, none of which could positively identify the compound as being di- or tetrabromide. The mass spectrum of the oil showed a pattern of peaks in the region m/z 398, indicative of the tetrabromide (272). The exact mass of 397.715016 confirmed the formula to be $\text{C}_6\text{H}_6\text{}^{79}\text{Br}_2\text{}^{81}\text{Br}_2$. However, further attempts to precipitate the tetrabromide and to obtain the material in a solid form proved to be unsuccessful. Trapping Dewar benzene with *m*-chloroperoxybenzoic acid by formation of the mono epoxide was also unsuccessful and no evidence for its formation could be found by ^1H -n.m.r. or mass spectroscopy.

Since it was difficult to form a stable adduct of Dewar benzene the isolation of Dewar benzene seemed the only alternative but these attempts of isolation by preparative g.l.c. at 45°C were unsuccessful. It is thought that further investigations into different bases for the Ramberg-Bäcklund reaction and the use of a more volatile solvent may provide a higher yield of Dewar benzene.

Finally as the method of synthesis of the α -chlorosulphone was found to be rather tedious a simpler method of providing an α -halosulphone was attempted. This method, devised by Becker *et al.*,⁸² involved the use of a Grignard reagent, as a base, with the sulphone (210) followed by the addition of bromine to

give the α -bromo sulphone (273) in 43% yield, as shown in Scheme 74.



Scheme 74

The bromosulphone (273) has not been used as a starting material for the Ramberg-Bäcklund reaction to form Dewar benzene so its ease of rearrangement cannot be commented upon.

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